Field-Effect-Transistor Characteristics of Solvate C$_{60}$ Fullerene Nanowhiskers

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Abstract. We demonstrate the operation of C$_{60}$ fullerene nanowhisker (FNW) field-effect transistors (FETs), realized by dissolving C$_{60}$ powder in either $m$-xylene or chlorobenzene solvents and performing liquid-liquid interface precipitation. There exists a clear dependence on solvent species for the FET performance. In contrast to prior studies, in which the FETs were investigated under vacuum conditions to avoid introducing crystalline disorder, we achieve comparable transistor operation for FETs under a N$_2$ atmosphere. The finding that solvate FNWs may be used to implement FETs could have important technological implications, by allowing practical applications of these materials to be developed.

1. Introduction

Organic thin-film field effect transistors (FETs) have been widely investigated in recent years, from the perspective of developing near-future device applications [1]. Among such materials, however, only a few show $n$-type characteristics in FET operation. C$_{60}$ is one of these materials, and improvements in its FET characteristics are therefore desired [2]. Recently, a novel approach for synthesizing fibrous C$_{60}$ crystals has been developed by using the method of liquid-liquid interface precipitation (LLIP). This yields C$_{60}$ fullerene nanowhiskers (FNWs) with uniform nanoscale cross-section, over lengths that can easily exceed several microns [3]. Previously, we reported on the fabrication of FET structures incorporating either multiple [4] or single [5] C$_{60}$ FNWs. For practical applications, it is desirable to be able to operate such FETs under ambient conditions. Unfortunately, however, the performance of C$_{60}$-based FETs is known to degrade on exposure to air, since adsorbed oxygen creates a deep trapping level that suppresses carrier transport [6]. Consequently, to date we have only succeeded in measuring the electrical characteristics of FNW FETs under vacuum conditions, after performing thermal annealing to remove oxygen and other adsorbates. One of the characteristics of C$_{60}$ FNWs synthesized by LLIP is that the as-grown, solvate C$_{60}$ crystals exhibit a hexagonal crystalline structure, in contrast to the face centered cubic (fcc) structure that is typical of C$_{60}$ films at room temperature (RT). The hexagonal structure is converted to the normal fcc one, however, after evaporating the solvent from the crystal, and this change in crystal structure is known to lead to the introduction of a high density of dislocations [7]. As a result, the C$_{60}$ FNW FETs that we have studied to date have typically suffered from pronounced crystalline disorder. In this work, however, we demonstrate an approach that allows us to achieve FET operation of FNW FETs in a nitrogen environment, without the need for vacuum isolation, thereby opening up the possibility of developing technological applications based on these devices.
2. Sample and experimental setup
The fabrication and structural characterization of the C_{60} FNWs we study was described in detail in a previous publication [4]. The process starts by preparing pure C_{60} powder by sublimation, in a vacuum chamber at a partial vacuum of order 10^{-6} Torr. The powder was then transferred into the N_{2} environment of a glove box without being exposed to air and was dissolved to saturation in either m-xylene or chlorobenzene, allowing us to compare the influence of these solvents on the resulting electrical characteristics. C_{60} NWs were then synthesized by the LLIP method, utilizing liquid phase separation between the C_{60} solution and isopropyl alcohol, during which the mixture was stored in a refrigerator at ~ 300 K for one week. The FET samples were fabricated on a 600-nm thick SiO_{2} layer on top of an n-type Si substrate and the source-drain electrodes were formed from Au with an adhesion layer of Ti. The device had a channel length (contact separation) of 5 µm and the FETs were formed by bridging these electrodes with several FNWs (Fig. 1 inset, for further information on this process, see [5]). To prevent contamination of the nanowhiskers by ambient oxygen, the critical steps of the device processing were prepared in a glove box filled with N_{2} gas. Subsequently, the FETs were installed into the chamber of a probe station without exposure to air. This allowed us to measure the room-temperature electrical properties of the solvate nanowhiskers directly. We were also able, however, to reduce the solvent content of these NWs, by pumping the sample chamber down to a vacuum of ~10^{-6} Torr. Under these conditions, we measured the characteristics of the dried FNWs, both before and after thermal annealing for a day at ~440 K. In experiments where the sample chamber was pumped to vacuum, a change of the crystalline structure of the C_{60} FNWs was confirmed by X-ray powder diffraction. As reported previously [4, 5], this change involves a transition from a well-defined hexagonal structure [8] to an fcc one whose diffraction peaks are broadened, indicating that the dried FNWs do not preserve the good crystallinity characteristic of the solvate condition. This change in crystalline character occurs even though the FNWs maintain their overall hexagonal cross-section [4, 5].

3. Results and discussion
In Fig. 1, we show the gate-voltage (V_{g}) characteristic of a C_{60} FNW FET, which was obtained by using the conducting substrate of the device as a back-gate (this accounts for the large values of this voltage). The LLIP process used to synthesize the FNW in this case involved the use of m-xylene solvent, and the measurements of Fig. 1 were obtained under the solvate condition due to the presence

![Figure 1. I_{ds} - V_{g} characteristic of a (m-xylene) C_{60} FNW FET measured under the solvate condition. The inset shows a scanning electron microscope image of the channel region of the FET.](image-url)
of a N$_2$ atmosphere. From the $V_g$ dependence of the source-drain current ($I_{sd}$), it can be inferred that the threshold voltage ($V_t$) and field-effect mobility ($\mu$) are $\approx 0$ V and $4 \times 10^{-5}$ cm$^2$/V s, respectively. (We determine the field mobility from the following relation for the source-drain current: $I_{sd} = (\mu W C_o / L) (V_g - V_t - \frac{1}{2} V_{sd}) V_{sd}$, where $W$, $L$, and $C_o$ are the FET channel width, length, and capacitance, respectively [5]). This device shows a normal-on characteristic similar to our former reports, with a mobility only a little lower than that which we have previously found [4] for dried FNW FETs (see Table 1). This represents the first important result of our study, since it demonstrates the possibility of obtaining FET action from FNWs under other than vacuum conditions.

Subsequent to the measurements of Fig. 1, the probe-station chamber was next evacuated to dry out the FNWs. After measuring the resulting FET characteristics, the device was then annealed at 440 K for 24 hours and cooled back down to RT. The resulting gate-voltage characteristics for these conditions are shown in Fig. 2. Note that the current in this figure is plotted on a logarithmic scale, for the solvate (curve (a)), dried (curve (b)), and dried and annealed (curve (c)), conditions. From these data it can be determined that $I_{sd} (V_g = 0)$ increases on evaporating the solvent, while the on/off ratio decreases from four- to two-orders of magnitude. On the other hand, we find that the mobility is improved to $10^{-2}$ cm$^2$/V s as a result of the annealing, an improvement of roughly a factor of two over the solvate condition.

We have also performed the same procedures as those described above, in this case for an FET whose channel was formed from FNWs realized using chlorobenzene as the solvent. The corresponding variations of $I_{sd}(V_g)$ measured in this case are shown in Fig. 3. From these data, we are again able to infer that the solvate FNW yields transistor characteristics that compare favourably with those obtained under vacuum conditions. The on-off ratio is a factor of ten larger in the solvate condition, but the inferred mobility is actually higher. These results are also summarized in Table 1, based on inspection of which we can make some further comments. In the solvate condition, it appears the mobility of the chlorobenzene-derived FNW is significantly enhanced over that of the $m$-xylene-derived one. Although the reasons for this are not completely understood, an important factor may be the different polar nature of the two solvents we have used. Specifically, Cl should act as a weak acceptor in chlorobenzene, while CH$_3$ acts as a donor in $m$-xylene with benzene. These results therefore suggest the importance of utilizing an appropriate solvent as a means to enhance the electrical characteristics of the solvate FNWs. The other noteworthy feature of Table 1 concerns the characteristics achieved after drying and annealing the FNWs. Since in this case the solvent is...
removed from the nanowhisker one might expect to obtain the same electrical characteristics for FNWs produced with either solvent. Table 1 confirms that the mobility and on-off ratios are the same in both cases. The threshold voltages are different, however, reflecting the unintentional doping induced by the different solvents.

Turning to the physical implications of our results, the observation of significant changes in the threshold voltage of both devices (Table 1) indicates that carriers are introduced into the FNWs, independent of the gate voltage, by evaporating the solvent. This may possibly be related to the introduction of a high density of dislocation and disorder [7], which could result in the creation of additional carriers in the FNWs. The low values of the mobility that we infer for both devices in the solvate condition appear reasonable, particularly in the case of \(m\)-xylene, since solvent molecules intercalated into the C\(_{60}\) crystal should extend the lattice constant, thereby decreasing the carrier hopping probability [9]. It is clear, on the other hand, that the mobility is not changed so systematically by removing the solvent from the nanowhiskers (compare the two different devices in Table 1). This may indicate some competition between the effect of eliminating the intercalated solvent molecules, and the ensuing increase in crystalline disorder when the crystalline structure of the FNWs undergoes a transition to the fcc form.

![Figure 3](image-url). \(I_{sd}V_g\) characteristic (with current plotted on a logarithmic scale) of a (chlorobenzene) C\(_{60}\) FNW FET, measured at room temperature under three different conditions: N\(_2\) atmosphere (solvate condition, filled circles), dried in vacuum (open circles), and dried in vacuum and annealed (open triangles).

### Table 1.

Caption: Summary of the results of measurement for the \(m\)-xylene and chlorobenzene C\(_{60}\) FNW FETs under different atmospheric conditions. The on-off ratio is determined as the ratio of currents at \(V_g = \pm 40\) V.

| Solvent     | Solvate Condition | Vacuum, Before Anneal | Vacuum, After Anneal |
|-------------|-------------------|-----------------------|----------------------|
|             | \(\mu\) (cm\(^2\)/Vs) | \(V_t\) (V) | On/Off Ratio | \(\mu\) (cm\(^2\)/Vs) | \(V_t\) (V) | On/Off Ratio | \(\mu\) (cm\(^2\)/Vs) | \(V_t\) (V) | On/Off Ratio |
| \(m\)-xylene| \(4 \times 10^{-3}\) | 0 | \(\sim 10^4\) | \(\sim 10^{-2}\) | \(< -40\) | \(\sim 10^2\) | \(\sim 10^{-3}\) | -13 | \(\sim 10^2\) |
| Chlorobenzene| \(5 \times 10^{-2}\) | 20 | \(\sim 10^3\) | \(\sim 10^{-2}\) | 0 | \(\sim 10^2\) | \(\sim 10^2\) | 0 | \(\sim 10^2\) |
4. Conclusion
In conclusion, we have demonstrated the operation of C_{60} FNW FETs under a N₂ environment, and have been able to achieve reasonable transistor action without the need to operate these devices under stringent vacuum conditions. The crystalline structure of the FNWs changes from an oriented hexagonal form to a disordered fcc one on evaporating the solvent. Accompanying this, resulting dislocations in the crystalline structure are believed to introduce carriers into the FNWs, thereby modifying the threshold gate voltage. The finding that solvate FNWs may be used to implement FETs could have important implications by allowing for technological applications of these materials to be developed. Future work should therefore focus on exploring suitable solvents for FNW fabrication to yield optimal electrical characteristics.

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