Air-stable \( n \)-channel single-crystal transistors with negligible threshold gate voltage

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Single-crystal transistors of highly electron-affine organic compounds were constructed on solid dielectrics to study intrinsic constraints for the \( n \)-channel field effect in ambient atmosphere. Tetracyanoquinodimethane field-effect devices reproducibly operate with a high mobility of 0.2–0.5 \( \text{cm}^2/\text{V} \cdot \text{s} \) in the air. The threshold gate voltage is negligible unlike most other air-stable \( n \)-type organic transistors reported, including polycrystal film devices of the same compound. Together with the other example of less electron-affine semiconductor crystal showing air-stable field effect but with notable threshold voltage, the result suggests that crucial in air-stable \( n \)-channel field effect is sufficient electron-affinity of the organic semiconductors. © 2009 American Institute of Physics.

Organic field-effect transistors (OFETs) have attracted considerable attention due to their applicability to flexible, low-cost, and large-area electronic devices. In particular, organic complementary devices are desired to be developed for extensive applications to organic logic circuits, where high-performance and air-stable OFETs of both \( p \)- and \( n \)-types are indispensable. For this purpose, the critical requirements for the construction of high-performance \( n \)-type OFETs, which operate stably in air have yet to be determined because there have been very few reports of such devices.1 Compared to \( p \)-type devices, air-stable \( n \)-type OFETs suffer from either low carrier mobility or very large threshold gate voltage, both of which severely limit their application as low-power complementary logic devices.

One proposed reason for the poorer performance of \( n \)-type OFETs is an energy-level mismatch between their Fermi levels and the lowest unoccupied molecular orbital (LUMO) levels of organic semiconductors. This would cause inefficient electron injection when noble metals are used as carrier-injecting electrodes. There are also concerns at the interfaces to the gate insulators, where the influence of the atmospheric oxidants \( \text{O}_2 \) and \( \text{H}_2\text{O} \) absorbed in grain boundaries of organic semiconductors, or \( \text{OH} \) groups at the surface of \( \text{SiO}_2 \), may also interfere with electron transport by acting as electron-trapping centers.2 In this study, OFETs based on \( n \)-type organic single crystals were employed to enable fundamental evaluation of the intrinsic device properties, eliminating the influences of grain boundaries and film morphology, as was done for \( p \)-type single cryystal OFETs.3–5 Noting that the highest reported mobility in air exceeds 20 \( \text{cm}^2/\text{V} \cdot \text{s} \) for rubrene single-crystal transistors,6,7 we sought the maximum performance of \( n \)-type OFETs in air. Air-stable \( n \)-type single-crystal 7,7,8,8-tetracyanoquinodimethane (TCNO) transistors exhibited high performance, with mobility values of 0.2–0.5 \( \text{cm}^2/\text{V} \cdot \text{s} \) and negligible threshold voltages, both of which are essential in the design of high-performance complementary devices. Remarkably, \( \text{SiO}_2 \), which has been believed to be very detrimental to \( n \)-type devices, was used for the above single-crystal transistors. This indicates that OH groups do not completely prevent the accumulation of electrons if the proper semiconductor materials are chosen.

A possible reason for the poorer performance of \( n \)-type OFETs is a performance closer to the intrinsic material performance of \( n \)-type OFETs can be achieved using single crystals, even under ambient atmosphere, as long as highly electron-affine semiconductors are employed.

In order to fabricate the bottom-contact \( n \)-type OFETs, thin plateletlike TCNO single crystals were grown to a thickness of 2–3 \( \mu \text{m} \) by physical vapor transport, then laminated by natural electrostatic force in air onto commercial \( \text{SiO}_2 \) (500 nm)/doped silicon substrates.4,5 Au electrodes were previously patterned on the substrate by photolithography. Figure 1(a) shows an optical-microscopic view of the TCNO single-crystal transistors. Measurements of transistor charac-

![FIG. 1. (Color online) (a) Optical view of the TCNO single-crystal transistor and (b) a circuit diagram of the four-terminal measurement.](image-url)
TCNQ thin-film transistors, indicating that the intrinsic material performance of n-type organic transistors suffers significantly from the effects of deep electron traps, resulting in poor performance or inoperability of n-type transistors. After tremendous recent efforts in the development of n-channel semiconductors, air-stable, high-mobility devices were reported recently.\textsuperscript{1,10–12} However, reports on transistors with $V_{th}$ of less than 10 V remain very rare and poorly reproducible.

To further understand the mechanism by which the threshold was minimized, we compared the results of other similarly prepared single-crystal transistors. As another example of air-stable n-type OFETs, we recently reported the much poorer performance of perylene tetracarboxylic dianhydride (PTCDA) single-crystal transistors. These had typical mobilities on the order of only $10^{-3}$ cm$^2$/V s, and $V_{th}$ was typically as high as 30–50 V.\textsuperscript{13} Since the LUMO level of PTCDA is reported to be 3.9 eV lower than vacuum level, which is 1 eV higher than that of TCNQ, it can be argued that PTCDA devices suffer from more severe barriers to electron injection, if one neglects energy-level renormalization at the interfaces due to such influences as interface dipoles. We also note that similarly prepared single-crystal transistors based on rubrene had an even lower LUMO level of $\sim$3.2 eV from vacuum level and did not function as n-type transistors in air. The comparison of transistor performances and electron affinities is given in Table I for the three single-crystal transistors.

In addition to the effect of electron-injection barriers at the gold-semiconductor interfaces, deep traps at the boundary to the gate insulators should also be considered. Since the effect of OH and water-based reactions are of concern, we also prepared TCNQ single-crystal devices with highly water-repellent amorphous fluoropolymer gate dielectrics that do not possess OH groups.\textsuperscript{14–16} The transistor characteristics exhibited were almost identical to those of the SiO$_2$ devices, indicating that the effects of electron trapping centers were minimal. As shown in Fig. 3, the trapping energies of such essential reductive processes appear to be located below the LUMO level of TCNQ, and above that of rubrene. This result is consistent with previous discussion of perylene-tetracarboxyldiimide derivatives,\textsuperscript{1} which used single-crystal transistors to avoid complications from grain boundaries. The report in Ref. 6 that some polymeric gate insulators, such as polydimethyl-siloxane or parylene, are very harmful to n-type transistor operation suggests that additional electron-trapping sites can be active, depending on the specific combination of materials. More extensive investigation is required to enable a full description of the reported observations.\textsuperscript{6}

![FIG. 3. Schematic illustration of the energy diagrams of Au Fermi level, LUMO levels of TCNQ and rubrene, and trapping energies.](Image)

### Table I. Performance of air-stable organic single-crystal transistors.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LUMO level (eV)</th>
<th>electron mobility (cm$^2$/V s)</th>
<th>threshold voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCNQ</td>
<td>4.8</td>
<td>$\sim$0.2–0.5</td>
<td>0</td>
</tr>
<tr>
<td>PTCDA</td>
<td>3.9</td>
<td>$\sim$10$^{-3}$</td>
<td>30–50</td>
</tr>
<tr>
<td>rubrene</td>
<td>3.2</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

*From the vacuum level.*
Finally, Fig. 4 exhibits the effect of surface modification by fluorinated self-assembled monolayers (F-SAMs). Because of finite polarization due to the dipole of the SAM molecules, the threshold voltage was slightly shifted. This observation is consistent with results from many other studies.17-18 In the present n-channel devices, the number of electrons was decreased by the polarization of the F-SAMs. As a result, the naturally electron-doped channel did not operate without $V_G$ application. A small negative $V_{th}$ of the devices without surface modification was reduced to nearly zero by the F-SAM treatment, demonstrating a method of controlling $V_{th}$ in low-power logic circuit devices.

In conclusion, organic single crystals of highly electron-affine molecules showed textbooklike transistor performance in air with high mobility, negligible hysteresis, and negligible threshold voltages, when complications resulting from grain boundaries and film morphology were excluded. The advantages of possessing a high electron affinity were not only a lowered electron-injection barrier from noble-metal electrodes. More importantly, oxidant components such as OH groups and water, which often act as electron-trapping centers, are deactivated because the LUMO levels of the semiconductor channels attract electrons more effectively. Therefore, these experiments demonstrate that the intrinsic material properties of highly electron-affine organic compounds enable high-performance, air-stable n-type transistors indispensable for the development of low-loss organic complementary circuits.

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