Single crystalline microribbons of perylo[1,12-*b*,*c*,*d*]selenophene for high performance transistors

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Micrometer sized single crystalline ribbons of a Se-heterocyclic annelated perylene were prepared by drop casting and physical vapor transport techniques. The crystals of the Se-heterocyclic annelated perylene showed near planar molecular conformation, which regularly stacked along *b*-axis with Se···Se contacts at 3.49 Å. Single crystal transistors of individual ribbon were fabricated by "gold layer glue" technique. Over 90% transistors exhibited mobility >1.6 cm^2 V^{-1} s^{-1}, the highest mobility approaching 2.66 cm^2 V^{-1} s^{-1}. The top performance indicated the bright prospect of this material in organic electronics. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3120769]

Organic field-effect transistors (OFETs) have recently received significant attention because of their potential applications in low-cost memories, smart cards, and driving circuits of large-area displays.[1–5] The rapid progresses of OFETs are approaching in two ways: the improvement of device fabrication techniques and the development of molecular semiconductors. The accomplished high performance OFETs are comparable to their inorganic counterpart, silicon-based transistors. A distinguished progress is the growth of high quality organic single crystals and their application in OFETs. As we know, organic single crystals are free of grain boundaries and are regarded as important candidates for the fabrication of high performance devices and in determining the structure-property relationship of organic semiconductors.[6–17] However, despite a great number of organic semiconductors have been evaluated and distinguished progresses have been achieved, there remains lack of (i) high mobility materials[6–20] and (ii) clear understanding of the relationship between crystal structure and field-effect mobility.[21,22] Moreover, organic crystals always exist as nanometer or micrometer sized "small" crystals. Inorganic microfabrication techniques such as electrobeam/focused ion beam depositions will damage or pollute organic crystals, which limit the application of the inorganic microfabrication techniques for organic single crystalline devices. Therefore, the fabrication of devices of the small organic crystals becomes a key challenge in organic electronics.[14,16,19]

Recently, we synthesized perylo[1,12-*b*,*c*,*d*]thiophene (PET).[23] The integration of a sulfur atom into the polycyclic aromatic hydrocarbon skeleton induced an extraordinary solid-state packing arrangement with the likelihood of double-channel superstructure. As we know, the transfer integral between the neighboring molecules affect the mobility of carriers. Therefore, it is believed that the mobility can be further enhanced with the replacement of sulfur atoms in the sulfur-annulated polycyclic aromatics with heavy chalcogen atoms such as selenium to enhance the molecular overlap integrals.[24–26] Unfortunately, up to now, selenium-comprising organic semiconductors are rarely addressed, not to mention their application in organic transistors. Herein, we reported the application of a Se-heterocyclic annelated perylene [inset of Fig. 1(a)] in OFETs. Single crystalline ribbons of the Se-heterocyclic annelated perylene at micrometer sized level were synthesized by drop casting and physical vapor transport techniques. The crystals of the compound showed nearly planar molecular conformation, which regularly stacked along *b*-axis in crystals with Se···Se contacts at 3.49 Å. OFETs of individual ribbon were fabricated, and high performances were demonstrated (with mobility reaching 2.66 cm^2 V^{-1} s^{-1}), which indicated the bright prospect of this material in organic electronics.

Perylo[1,12-*b*,*c*,*d*]selenophene (PESE) was synthesized in high yield by a surprisingly simple one-pot procedure from the readily available one-nitroperylene.[27] The key step was carried out in N-methylpyrrolidone with selenium powder at 180 °C in 5 h, following standard purification to give the desired product in 65% yield. Microribbons of

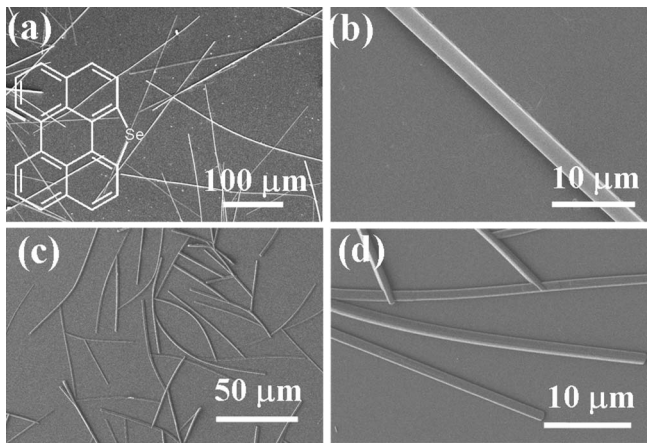

FIG. 1. SEM images of the PESE microribbons grown by drop casting [(a) and (b)] and physical vapor transport [(c) and (d)] on the SiO_2/Si substrate with OTS treatment.

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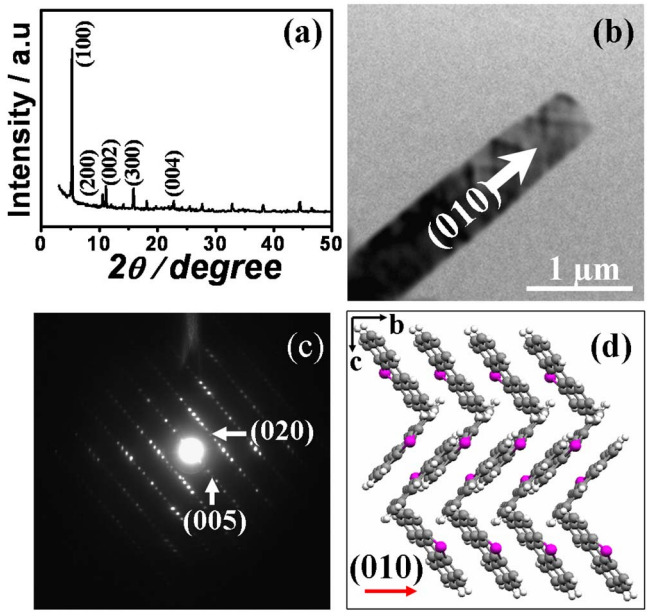

FIG. 2. (Color online) (a) XRD experimental results for the PESE microribbons, [(b) and (c)] TEM images of a single-crystal PESE wire and its corresponding electron diffraction pattern, and (d) view down the crystallographic *a*-axis.

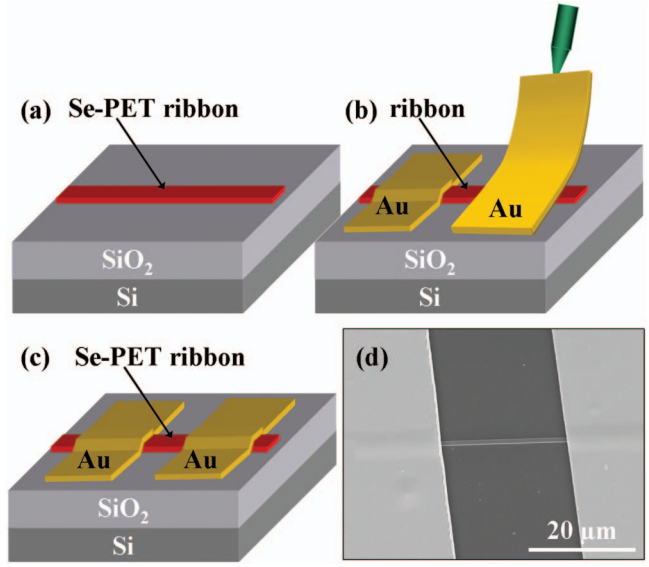

FIG. 3. (Color) [(a)–(c)] The schematic for the fabrication of the single crystalline ribbon transistors and (d) SEM image of a transistor based on an individual ribbon, the channel length of the device was 23.7 μm, and the width was 0.86 μm (width of the ribbon).

PESE were prepared both by solution processed and physical vapor transport techniques. For solution processed technique, a saturated solution of PESE in toluene was prepared and poured over the *n*-octadecyltrichlorosilane (OTS)-treated SiO_2/Si substrates directly,[28] then keep the substrates in the Petri dishes at room temperature at least for 24 h; after the solvent evaporation, long, thin microribbons were obtained on substrates as shown in Fig. 1(a). Most of the ribbons with length approached several hundreds micrometers and width one to several micrometers as shown in Fig. 1(b). The physical vapor transport technique was carried out using a two-zone horizontal tube furnace.[29] A quartz boat loaded with powders of PESE was placed at the high-temperature zone (138 °C). High pure Ar was used as the carrier gas and the system was evacuated by a mechanical pump. Products were obtained at the low-temperature zone (45 °C). The products were shown in Fig. 1(c). Most of the ribbons with length ranged from several tens to 100–200 μm and diameter at several micrometers as shown in Fig. 1(d).

The powder x-ray diffraction (XRD) patterns of the products were shown in Fig. 2(a). All the diffraction peaks could be indexed unambiguously to the monoclinic structures ($P2_1/C$).[30] Figure 2(b) showed a transmission electron microscopy (TEM) image of a representative single-crystalline PESE microribbon, and Fig. 2(c) showed selected area electron diffraction (SAED) pattern obtained from the same microribbon. The highly crystalline nature of the PESE microribbons was confirmed by the SAED pattern, which was recorded perpendicular to the microribbon long axis. The SAED pattern was indexed with lattice constants obtained from the single crystalline XRD data: $a=18.073$ Å, $b=4.429$ Å, $c=17.102$ Å, $\alpha=90.00°$, $\beta=113.396°$, and $\gamma=90.00°$. It could be concluded that the single-crystalline PESE microribbon grew along the [010] direction, which coincided with the π-π stacking direction of the PESE molecules [Fig. 2(d)]. Moreover, the Se···Se contacts of PESE were at around 3.49 Å, which were shorter than that of *S*···*S* short contacts 3.51 Å of PET molecules, indicating a more compressed molecular packing structure. This extraordinary double-channel superstructure of π-π and Se···Se contacts made PESE attractive candidate for devices.

As we know, the conducting channel of organic transistors is just located at the interface of semiconductor and insulator, hence, an important aspect influencing the device performance is the contact between semiconductor and gate insulator. In order to guarantee the intimate contact of the single crystalline ribbons with SiO_2 insulator, the ribbons of PESE were *in situ* patterned onto the *n*-OTS-treated SiO_2/Si substrates by physical vapor transport technique with nanocrystalline seeds selective growth.[31] Briefly, PESE crystalline nuclei at nanometer size were predeposited on OTS modified SiO_2/Si substrates. Then, the substrates were transferred into physical vapor transport system to grow PESE ribbons. In this way, PESE ribbons could grow from the predeposited PESE nuclei into long ribbons, and the ribbons were just extended along the surface of the substrate. This *in situ* patterning process was free from surface pollution and mechanical damage, and provided an intimate $PESE/SiO_2$-OTS contact for high quality crystal/insulator interface. After that, the electrodes of the transistors, source and drain layer slices, were glued onto the ribbon operated by a mechanical probe.[32] The Au layers were prepared as follows: first, Au thin film with a thickness of ~100 nm was predeposited on a Si wafer by thermal evaporation. Then, a small piece of the Au film, approximately 30×150 μm^2, was peeled off the Si substrate with the tip of the mechanical probe and transferred onto the microribbon as a source or drain electrode. The devices fabrication could be depicted by Figs. 3(a) and 3(b). The conventional method for the fabrication of electrodes is by vacuum deposition or sputtering. On one hand, during the vacuum deposition or sputtering, the high-temperature and high-energy metal atoms will seriously damage the crystalline surface to degrade the device performance.[33,34] On the other hand, during the deposition process, the metal atoms easily fill the pinholes in the dielectric, causing high leakage current.[35,36] These factors may conceal the properties of the

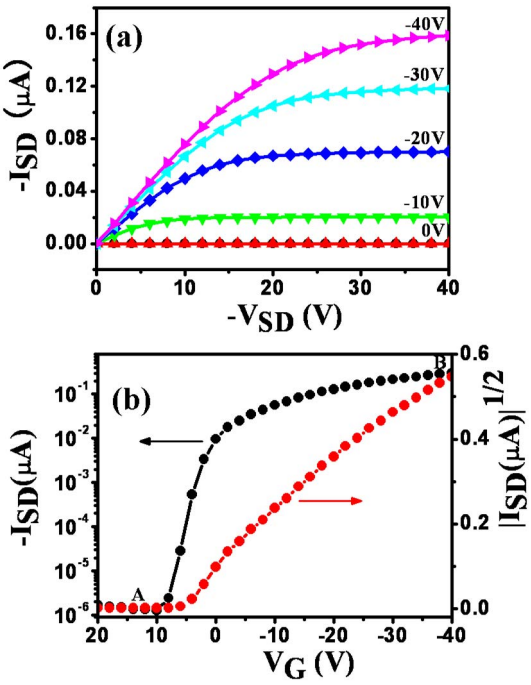

FIG. 4. (Color online) Output (a) and transfer (b) characteristics of single-crystal OFETs of individual ribbon with mobility at 2.66 $cm^2\ V^{-1}\ s^{-1}$ and on/off ratio at 2.3×10^5.

organic materials, and may even cause a failure of the organic device, in particular, small-sized organic single crystal devices.[37] Here, our mechanical devices fabrication processes could avoid these disadvantages to provide a possibility for the fabrication of high performance devices.

The representative output and transfer characteristics of the devices based on individual single crystal ribbon were shown in Fig. 4. All devices exhibited typical *p*-type transistor behavior. Moreover, the devices exhibited very weak hysteresis as shown in the transfer curves indicating the reducing of charge trapping effects, i.e., the high quality of the small interface between the *in situ* patterned single crystalline ribbon and OTS modified SiO_2 insulator. The highest mobility of the devices was calculated at 2.66 $cm^2\ V^{-1}\ s^{-1}$ with on/off ratio at 2.3×10^5. Attractively, all examined devices exhibited mobility larger than 1.0 $cm^2\ V^{-1}\ s^{-1}$, over 90% devices with mobility over 1.6 $cm^2\ V^{-1}\ s^{-1}$. It is undoubtedly suggested PESE is an attractive candidate for organic/molecular electronics.

In conclusion, single crystalline micrometer sized ribbons of a compound of Se-heterocyclic annelated perylene were synthesized by poured cast or physical vapor transport techniques. The crystals of the Se-heterocyclic annelated perylene showed near planar molecular conformation, which regularly stacked along *b*-axis with a compressed molecular packing structure, i.e., the Se···Se contacts at 3.49 Å. Single crystal transistors of individual ribbon were fabricated by gold layer glue technique. All examined devices exhibited mobility larger than 1.0 $cm^2\ V^{-1}\ s^{-1}$, over 90% devices with mobility over 1.6 $cm^2\ V^{-1}\ s^{-1}$, the highest mobility approached 2.66 $cm^2\ V^{-1}\ s^{-1}$. It is undoubtedly suggested the shorter Se···Se contacts (3.49 Å) is favorable for efficient carrier transport, i.e., for high mobility, and Se-heterocyclic annelated perylene is an attractive candidate for organic/molecular electronics.

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