Thermoelectric transport at F$_4$TCNQ—silicon interface

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Abstract: Hybrid organic-inorganic materials are among the latest class of materials proposed for thermoelectric applications. The organic-inorganic interface is critical in determining the effective transport properties of the hybrid material. We study the thermoelectric properties of the F$_4$TCNQ—silicon interface. Transfer of electrons from silicon to F$_4$TCNQ results in holes trapped within the screening length of the interface that can move parallel to the interface. We measure the response of these trapped charges to applied temperature differential and compare the thermoelectric transport properties of the silicon with and without F$_4$TCNQ. The results confirm the presence of interface charges and demonstrate enhanced interface thermoelectric power factor. These outcomes of this study could be used in designing 3D hybrid structures with closely packed interfaces to replicate a bulk thermoelectric material.
Interfaces play a key role in semiconductor devices. The electron transport at conducting interfaces is of importance in the design of high-electron-mobility-transistors, superlattice structure devices, and energy conversion materials such as photovoltaics and thermoelectric materials. In particular, novel hybrid organic-inorganic materials have drawn increasing attention in research for diverse range of applications in energy, environment and healthcare.

This work focuses on the charge transfer at an organic-inorganic interface, which shows promise in designing transfer-doped semiconductor nano-devices. Conventional doping methods (e.g. ion implantation) are oftentimes destructive processes introducing excess defects. The activation process ubiquitously requires solid-state thermal diffusion, which cannot be applied to materials that are heat sensitive. Devices with ultrafine structures would also suffer from non-negligible statistical variation or deactivation of dopants. The other main drawback of conventional doping methods is that they all involve incorporating aliovalent impurity ions, which create long range Coulomb potentials that scatter conduction electrons and lowers their mobility. Modulation doping or remote doping has been proposed for 2D structures to overcome these shortcomings and has been implemented in transistor technology. Over 22 years (from 1978 to 2000), mobility enhancement by 4 orders of magnitude have been reported in GaAs, which was achieved by spatially separating parent atoms from conduction electrons. Another alternative doping strategy is surface doping of inorganic semiconducting materials by organic molecules, which was proposed fairly recently. Both in modulation doping and surface doping, charge carriers are confined to the interface of organic-inorganic materials and form a 2D electron gas (2DEG). To extend the advantages of 2DEG to 3D devices, one can envision forming superlattice structures by alternating organic-inorganic layers. Such hybrid superlattices have been theoretically evaluated for thermoelectric applications. Alternative 3D structures such as nanoparticles, nanowires and
holes embedded in host matrices, specifically for thermoelectric applications have been proposed and discussed in detail.\textsuperscript{23–28}

In this work, we fabricated a device to investigate the charge transfer of tetrafluorotetracyanoquinodimethane (F\textsubscript{4}TCNQ) – silicon interface. F\textsubscript{4}TCNQ is a fluorinated TCNQ derivative, and has an exceptionally high electron affinity of $E_a = 5.24\text{eV}$.\textsuperscript{29} It’s well known as a strong electron acceptor, to dope molecules p-type by forming charge transfer organic complex, as well as to enhance hole injection by energy level alignment at organic – metal interfaces.\textsuperscript{30,31} Therefore, F\textsubscript{4}TCNQ has been widely applied in organic light emitting diodes (OLEDs),\textsuperscript{32,33} photovoltaics,\textsuperscript{34,35} organic field-effect transistors (OFETs),\textsuperscript{36} etc. P-type surface doping was also achieved at inorganic semiconductor surfaces, such as diamond\textsuperscript{37}, graphene\textsuperscript{38}, and VO\textsubscript{2}\textsuperscript{39}, and investigated by photoemission spectroscopy (PES) techniques. However, as the most pervasive semiconductor material for electronic devices, Si, has only sparsely been examined experimentally as the active layer for transfer doping by F\textsubscript{4}TCNQ. Existing reports mainly focus on electronic structure study by PES\textsuperscript{40–42} without details on the resultant transport properties. Therefore, we seek to investigate the electrical transport properties of the F4TCNQ-Si interface. The lowest unoccupied state (LUMO) of F\textsubscript{4}TCNQ lies below the silicon valence band maximum (VBM), hence the electron affinity of F\textsubscript{4}TCNQ is larger than the ionization energy of Si (Fig. 1 a)). This favors electron-transfer from silicon to F\textsubscript{4}TCNQ molecules, and Si is thus p-type doped near the interface. The holes are confined in the direction normal to the interface due to the established electrostatic potential but free to move in the parallel direction. XPS study shows that the shift of Si 2p binding energy peak saturates when the in-situ deposited F\textsubscript{4}TCNQ thickness is 2 nm\textsuperscript{43}, meaning the F\textsubscript{4}TCNQ molecules farther to the interface do not contribute to the charge transfer, as illustrated in Fig. 1 b). Our previous calculation indicated that physisorbed F\textsubscript{4}TCNQ self-
assembled monolayers can efficiently dope silicon, achieving hole concentrations as high as $10^{13}$ cm$^{-2}$.\textsuperscript{44}

A combination of enhanced mobility by transfer doping and low thermal conductivity of F$_4$TCNQ could be utilized to design a high performance F$_4$TCNQ – nanostructured Si (e.g. nanopatterned holey Si or nanowires) hybrid thermoelectric materials. However, this concept relies on a fundamental understanding of charge transfer and thermoelectric transport at the interface of F$_4$TCNQ – silicon, which is thereby the main focus of this work.

In order to make a device to measure the interface properties we built a silicon channel as shown in Figure 2. The device Si(100) layer (4'' SOI with 2 \(\mu\)m BOX) was thinned down to \(\sim\)100nm by reactive ion etching (RIE). The subsequent blanket boron implantation yielded a mild hole concentration \(\sim10^{16}\) cm$^{-3}$ in the Si layer. Four side contact (5 \(\mu\)m \(\times\) 20 \(\mu\)m) areas were then exposed by resist and underwent another boron implantation process, which yielded \(\sim10^{20}\) cm$^{-3}$ only in the contact areas. The Si layer was etched down to BOX to form arrays of 30 \(\mu\)m \(\times\) 200 \(\mu\)m Si mesas for the following metallization. 1\(\mu\)m Al with 50nm Au cap was deposited as contacts for transport measurements. The device configuration is shown in Fig. 2. The heater, thermometers and contacts are annotated. Finally, rapid thermal annealing was conducted at 500 °C for 30s to achieve Ohmic contact.

Next, we deposited F$_4$TCNQ on the silicon device by thermal evaporation. The thermometers and the electrodes are then in between the Silicon and F$_4$TCNQ allowing us to characterize the interface. F$_4$TCNQ is insulating. Despite withdrawing electrons from Si upon contact, the electrical conduction of the F$_4$TCNQ film is negligible compared to the Si layer. Therefore, it was feasible to directly deposit F$_4$TCNQ onto the metallized device, without shorting the metal lines. Prior to the deposition, the device was dipped in BOE for 25 seconds to create a passive H-terminated Si
surface, in order to prevent charge confinement by the surface states. The metal pads were then covered by a shadow mask for the ease of wire bonding after deposition. The F$_4$TCNQ crystal powder (Sigma-Aldrich, 99.9%) and the device were loaded into a homebuilt miniature thermal evaporation chamber with a base pressure of $<10^{-6}$ torr. F$_4$TCNQ was degassed below 100°C and then sublimated at 140°C for deposition. Surface morphology was characterized by atomic force microscopy (AFM). The XTEM sample with F$_4$TCNQ/Si interface was prepared by a focused ion beam (FIB) lift-out process, and the interface morphology was then characterized by transmission electron microscopy (TEM) along Si [110]. The electrical resistance was measured using four-point probe method, both before and after depositing F$_4$TCNQ. The Seebeck coefficient was measured in a homebuilt 2D transport measurement system incorporated in a Janis cryostat.

It was found that the F$_4$TCNQ has a relatively low sticking probability on H-Si(100), which is commonly observed for molecules physical adsorbed on inorganic substrate$^{45}$. Furthermore, due to the limited wettability, F$_4$TCNQ adsorbates tend to coalesce into densely-packed islands on Si.

In order to achieve full coverage and maximize the charge transfer, a relatively high vapor flux is required to create a high nucleation rate. Therefore, we used a higher F4TCNQ temperature of ~140°C compared to other PES studies$^{40-42}$. The net deposition rate was calibrated as ~ 1.5Å/s. Figure 3 shows the surface morphology of F$_4$TCNQ with root mean square (RMS) roughness of ~17 nm under this deposition condition.

The interface is investigated by XTEM, as shown in Fig. 4. The active Si layer is ~100nm in thickness, on a 2μm buried oxide layer, so that the subsequent transport measurements are minimally affected by the substrate. As shown in Fig.4 a), continuous coverage of F$_4$TCNQ on Si
was achieved, with an average thickness of ~150nm. In essence, only the first few layers of molecule would contribute to the charge transfer, leaving the majority as neutral $F_4$TCNQ bulk. Figure 4 b) is the high-resolution image along Si [110] axis. It exhibits a smooth interface without observable voids or interlayers. Therefore, an effective charge transfer can be expected across the interface. Nevertheless, the orientation of molecules on Si surface is still unclear, which could affect the transfer doping efficiency\(^4\). Future work using STM\(^4\) or PES\(^4\) techniques may shed light on orientation of the molecules.

In order to evaluate the charge transfer, and its effect on power factor, we performed electrical transport measurements. I-V measurements by the 4-probe method were conducted first on the mildly p-doped, uncoated Si device, and then on the same device deposited with $F_4$TCNQ. As shown in Fig. 5, Ohmic IV curves were achieved in both cases. The measured resistance of $F_4$TCNQ – Si (401kΩ) is 10 times lower compared to the resistance of plain Si device (4.36 MΩ). The result provides a direct evidence that charge transfer at the interface occurred and that silicon is surface doped by the physically adsorbed $F_4$TCNQ.

The Seebeck coefficient was then measured using a micro heater and two calibrated thermometers, as shown in Fig. 2. When applying a current to the heater, a temperature difference is built up across the two ends of the Si mesa as a result of joule heating inside the heater. Therefore, an electrical potential is produced due to Seebeck effect. Since the thermometers are in direct contact with Si surface, the Seebeck voltage could thereby be measured. We observe a large drop in the Seebeck voltage from -208.9 ± 12.3 μV for mildly doped, uncoated Si to -73.9 ± 3.7 μV after deposition of $F_4$TCNQ (see the steady state voltage shown in Fig. 6 a). In order to extrapolate the actual Seebeck coefficient ($S = -\frac{V_S}{\Delta T}$), the corresponding temperature differential must be measured. The temperature of the device could be extracted from the temperature-dependent
resistance of the thermometers. Separate temperature calibrations were conducted for each thermometer. The sample’s temperature was raised using an external heater in the sample holder and the resistance of the thermometers was measured versus temperature. A minor increase of thermometer resistance after depositing F₄TCNQ was noted due to the presence of the molecules on the gold lines and therefore their resistances were recalibrated afterwards.

During the Seebeck measurement, when the heater turns on, the resistance (by 4-point method) of the thermometers ramps up as shown in Fig. 6 b) – e). Using the calibration curves, we could then extrapolate the ΔT (TC₁ – TC₂), which reached to a steady state after ~ 20 seconds, corresponding to the Seebeck voltage plateau. The Seebeck coefficients determined by this approach for the uncoated Si device is 594.6 ± 38.0 μV/K, and for F₄TCNQ – Si device is 243 ± 12.3 μV/K. The sign of Seebeck coefficients confirms that both devices are p-type doped. It was found that the power factor (S²/R) of silicon had a 75% enhancement after depositing F₄TCNQ.

Since the screening length of surface-doped holes is estimated to be less than 10 nm, the majority of the coated device is not contributing to the conductance. Given that the resistance had 10 times’ reduction, and carrier mobility should be unchanged in F₄TCNQ – Si, a ~100 times enhancement in hole concentration can be estimated in the modulation doped region in proximity to the interface.

The obtained Seebeck value of 243 ± 12.3 μV/K for F₄TCNQ – Si sample, could be interpreted as the Seebeck coefficient of the 2D hole gas since the transferred charge accumulated near the surface is the dominant contributor to the Seebeck voltage. The thermal conductivity is not affected and we estimated a similar thermal resistance with and without F₄TCNQ since in this case, measurements are done for the interface and lattice thermal conductance of silicon is the dominant heat transfer mechanism.
These results serve as a proof of concept of the potential of organic – Si interfaces with large charge transfer for power factor optimization for thermoelectric device application. The issue of limited conductance enhancement due to the short screening length brings in the necessity of having nanostructured Si with high surface-to-volume ratio (e.g. nanopatterned holey Si), in which case the transfer doping can be maximized, and the necking size is comparable to the screening length of transferred charges so as to freely transport throughout the material. Future study on manipulating the molecule orientation, and surface treatment to minimize surface states as charge trap is expected to further enhance the power factor.

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Reference

(1) Asif Khan, M.; Bhattarai, A.; Kuznia, J. N.; Olson, D. T. High Electron Mobility Transistor Based on a GaN-AlxGa1-xN Heterojunction. Appl. Phys. Lett. 1993, 63, 1214–1215.

(2) Zhang, Y.; Singh, J. Charge Control and Mobility Studies for an AlGaN/GaN High Electron Mobility Transistor. J. Appl. Phys. 1999, 85, 587–594.

(3) Hori, Y.; Yatabe, Z.; Hashizume, T. Characterization of Interface States in Al2O3/AlGaN/GaN Structures for Improved Performance of High-Electron-Mobility Transistors. J. Appl. Phys. 2013, 114.

(4) Feenstra, R. M.; Collins, D. A.; Ting, D. Z. Y.; Wang, M. W.; McGill, T. C. Interface Roughness and Asymmetry in InAs/GaSb Superlattices Studied by Scanning Tunneling Microscopy. Phys. Rev. Lett. 1994, 72, 2749–2752.

(5) Haigh, S. J.; Gholinia, A.; Jalil, R.; Romani, S.; Britnell, L.; Elias, D. C.; Novoselov, K. S.; Ponomarenko, L. A.; Geim, A. K.; Gorbachev, R. Cross-Sectional Imaging of Individual Layers and Buried Interfaces of Graphene-Based Heterostructures and Superlattices. Nat. Mater. 2012, 11, 764–767.

(6) Chowdhury, I.; Prasher, R.; Lofgreen, K.; Chrysler, G.; Narasimhan, S.; Mahajan, R.; Koester, D.; Alley, R.; Venkatasubramanian, R. On-Chip Cooling by Superlattice-Based Thin-Film Thermoelectrics. Nat. Nanotechnol. 2009, 4, 235–238.

(7) Goh, C.; Scully, S. R.; McGehee, M. D. Effects of Molecular Interface Modification in Hybrid Organic-Inorganic Photovoltaic Cells. J. Appl. Phys. 2007, 101.

(8) Huanping Zhou, Qi Chen, Gang Li, Song Luo, Tze-bing Song, Hsin-Sheng Duan, Ziruo Hong, Jingbi You, Yongsheng Liu, Y. Y. Interface Engineering of Highly Efficient Perovskite Solar Cells. Science (80-. ). 2014, 345, 542–546.

(9) Schulz, P.; Edri, E.; Kirmayer, S.; Hodes, G.; Cahen, D.; Kahn, A. Interface Energetics in Organo-Metal Halide Perovskite-Based Photovoltaic Cells. Energy Environ. Sci. 2014, 7, 1377–1381.

(10) Medlin, D. L.; Snyder, G. J. Interfaces in Bulk Thermoelectric Materials. A Review for Current Opinion in Colloid and Interface Science. Curr. Opin. Colloid Interface Sci. 2009, 14, 226–235.

(11) Sungtaek Ju, Y.; Ghoshal, U. Study of Interface Effects in Thermoelectric Microrefrigerators. J. Appl. Phys. 2000, 88, 4135.

(12) Dresselhaus, M. S.; Chen, G.; Tang, M. Y.; Yang, R. G.; Lee, H.; Wang, D. Z.; Ren, Z. F.; Fleurial, J.-P.; Gogna, P. New Directions for Low-Dimensional Thermoelectric Materials. Adv. Mater. 2007, 19, 1043–1053.

(13) Hybrid Organic-Inorganic Interfaces : Towards Advanced Functional Materials; Delville, Marie Helene, Taubert, A., Ed.; WILEY-V C H VERLAG GMBH, 2017.

(14) Rietwyk, K. J.; Smets, Y.; Bashouti, M.; Christiansen, S. H.; Schenk, A.; Tadich, A.; Edmonds, M. T.; Ristein, J.; Ley, L.; Pakes, C. I. Charge Transfer Doping of Silicon. Phys. Rev. Lett. 2014, 112, 1–5.

(15) Björk, M. T.; Schmid, H.; Knoch, J.; Riel, H.; Riess, W. Donor Deactivation in Silicon Nanostructures. Nat. Nanotechnol. 2009, 4, 103–107.

(16) Dingle, R.; Störmer, H. L.; Gossard, A. C.; Wiegmann, W. Electron Mobilities in Modulation-Doped Semiconductor Heterojunction Superlattices. Appl. Phys. Lett. 1978, 33, 665.
(17) Pfeiffer, L.; West, K. The Role of MBE in Recent Quantum Hall Effect Physics Discoveries. *Phys. E Low-dimensional Syst. Nanostructures* **2003**, *20*, 57–64.

(18) Ristein, J. Surface Transfer Doping of Semiconductors. *Science (80-.)*. **2006**, *313*, 1057–1058.

(19) Chen, W.; Qi, D.; Gao, X.; Wee, A. T. S. Surface Transfer Doping of Semiconductors. *Prog. Surf. Sci.* **2009**, *84*, 279–321.

(20) Lee, D.; Sayed, S. Y.; Lee, S.; Kuryak, C. A.; Zhou, J.; Chen, G.; Shao-Horn, Y. Quantitative Analyses of Enhanced Thermoelectric Properties of Modulation-Doped PEDOT:PSS/undoped Si (001) Nanoscale Heterostructures. *Nanoscale* **2016**, *8*, 19754–19760.

(21) Lee, D.; Zhou, J.; Chen, G.; Shao-Horn, Y. Enhanced Thermoelectric Properties for PEDOT:PSS/Undoped Ge Thin-Film Bilayered Heterostructures. *2018*, *1800624*, 1–11.

(22) Carrete, J.; Mingo, N.; Tian, G.; Ågren, H.; Baev, A.; Prasad, P. N. Thermoelectric Properties of Hybrid Organic–Inorganic Superlattices. *J. Phys. Chem. C* **2012**, *116*, 10881–10886.

(23) Yu, B.; Zebarjadi, M.; Wang, H.; Lukas, K.; Wang, H.; Wang, D.; Opeil, C.; Dresselhaus, M.; Chen, G.; Ren, Z. Enhancement of Thermoelectric Properties by Modulation-Doping in Silicon Germanium Alloy Nanocomposites. *Nano Lett.* **2012**, *12*, 2077–2082.

(24) Zebarjadi, M.; Joshi, G.; Zhu, G.; Yu, B.; Minnich, A.; Lan, Y.; Wang, X.; Dresselhaus, M.; Ren, Z.; Chen, G. Power Factor Enhancement by Modulation Doping in Bulk Nanocomposites. *Nano Lett.* **2011**, *11*, 2225–2230.

(25) Zebarjadi, M.; Chen, G.; Ren, Z.; Shin, S.; Chen, R.; Heremans, J. P.; Wiendlocha, B.; Jin, H.; Wang, B.; Zhang, Q. Engineering of Materials. In *Advanced thermoelectrics: materials, contacts, devices and systems*; Ren, Z.; Lan, Y.; Zhang, Q., Eds.; CRC Press, 2018.

(26) Song, E.; Li, Q.; Swartenzuber, B.; Pan, W.; Wang, G. T.; Martinez, J. A. Enhanced Thermoelectric Transport in Modulation-Doped GaN/AlGaN Core/shell Nanowires. *Nanotechnology* **2016**, *27*, 15204.

(27) Wang, H.; Cao, X.; Takagiwa, Y.; Snyder, G. J. Higher Mobility in Bulk Semiconductors by Separating the Dopants from the Charge-Conducting Band – a Case Study of Thermoelectric PbSe. *Mater. Horiz.* **2015**, *2*, 323–329.

(28) Bahk, J.-H.; Bian, Z.; Zebarjadi, M.; Santhanam, P.; Ram, R.; Shakouri, A. Thermoelectric Power Factor Enhancement by Ionized Nanoparticle Scattering. *Appl. Phys. Lett.* **2011**, *99*, 72118.

(29) Gao, W.; Kahn, A. Electronic Structure and Current Injection in Zinc Phthalocyanine Doped with Tetrafluorotetracyanoquinodimethane: Interface versus Bulk Effects. *Org. Electron. physics, Mater. Appl.* **2002**, *3*, 53–63.

(30) Koch, N.; Duhm, S.; Rabe, J. P.; Vollmer, A.; Johnson, R. L. Optimized Hole Injection with Strong Electron Acceptors at Organic-Metal Interfaces. *Phys. Rev. Lett.* **2005**, *95*, 4–7.

(31) Braun, S.; Salaneck, W. R.; Fahlman, M. Energy-Level Alignment at Organic/metal and Organic/organic Interfaces. *Adv. Mater.* **2009**, *21*, 1450–1472.

(32) Blochwitz, J.; Pfeiffer, M.; Fritz, T.; Leo, K. Low Voltage Organic Light Emitting Diodes Featuring Doped Phthalocyanine as Hole Transport Material. *Appl. Phys. Lett.* **1998**, *73*, 729–731.

(33) Huang, J.; Pfeiffer, M.; Werner, A.; Blochwitz, J.; Leo, K.; Liu, S. Low-Voltage Organic
Electroluminescent Devices Using Pin Structures. *Appl. Phys. Lett.* **2002**, *80*, 139–141.

(34) Yim, K.-H.; Whiting, G. L.; Murphy, C. E.; Halls, J. J. M.; Burroughes, J. H.; Friend, R. H.; Kim, J.-S. Controlling Electrical Properties of Conjugated Polymers via a Solution-Based P-Type Doping. *Adv. Mater.* **2008**, *20*, 3319–3324.

(35) Liu, D.; Li, Y.; Yuan, J.; Hong, Q.; Shi, G.; Yuan, D.; Wei, J.; Huang, C.; Tang, J.; Fung, M. K. Improved Performance of Inverted Planar Perovskite Solar Cells with F4-TCNQ Doped PEDOT:PSS Hole Transport Layers. *J. Mater. Chem. A* **2017**, *5*, 5701–5708.

(36) Soeda, J.; Hirose, Y.; Yamagishi, M.; Nakao, A.; Uemura, T.; Nakayama, K.; Uno, M.; Nakazawa, Y.; Takimiya, K.; Takeya, J. Solution-Crystallized Organic Field-Effect Transistors with Charge-Acceptor Layers: High-Mobility and Low-Threshold-Voltage Operation in Air. *Adv. Mater.* **2011**, *23*, 3309–3314.

(37) Qi, D.; Chen, W.; Gao, X.; Wang, L.; Chen, S.; Kian, P. L.; Wee, A. T. S. Surface Transfer Doping of Diamond (100) by Tetrafluoro-Tetracyanoquinodimethane. *J. Am. Chem. Soc.* **2007**, *129*, 8084–8085.

(38) Chen, W.; Chen, S.; Dong, C. Q.; Xing, Y. G.; Wee, A. T. S. Surface Transfer P-Type Doping of Epitaxial Graphene. *J. Am. Chem. Soc.* **2007**, *129*, 10418–10422.

(39) Wang, K.; Zhang, W.; Liu, L.; Guo, P.; Yao, Y.; Wang, C. H.; Zou, C.; Yang, Y. W.; Zhang, G.; Xu, F. Holes Doping Effect on the Phase Transition of VO2 Film via Surface Adsorption of F4TCNQ Molecules. *Appl. Surf. Sci.* **2018**, *447*, 347–354.

(40) Mukai, K.; Yoshinobu, J. Observation of Charge Transfer States of F4-TCNQ on the 2-Methylpropene Chemisorbed Si(1 0 0)(2 × 1) Surface. *J. Electron Spectros. Relat. Phenomena* **2009**, *174*, 55–58.

(41) Furuhashi, M.; Yoshinobu, J. Charge Transfer and Molecular Orientation of Tetrafluoro-Tetracyanoquinodimethane on a Hydrogen-Terminated Si(111) Surface Prepared by a Wet Chemical Method. *J. Phys. Chem. Lett.* **2010**, *1*, 1655–1659.

(42) Yoshimoto, S.; Furuhashi, M.; Koitaya, T.; Shiozawa, Y.; Fujimaki, K.; Harada, Y.; Mukai, K.; Yoshinobu, J. Quantitative Analysis of Chemical Interaction and Doping of the Si(111) Native Oxide Surface with Tetrafluorotetracyanoquinodimethane. *J. Appl. Phys.* **2014**, *115*.

(43) Yuan, G. D.; Ng, T. W.; Zhou, Y. B.; Wang, F.; Zhang, W. J.; Tang, Y. B.; Wang, H. B.; Luo, L. B.; Wang, P. F.; Bello, I.; *et al.* P-Type Conductivity in Silicon Nanowires Induced by Heterojunction Interface Charge Transfer. *Appl. Phys. Lett.* **2010**, *97*, 95–98.

(44) Wang, X.; Esfarjani, K.; Zebardi, M. First-Principles Calculation of Charge Transfer at the Silicon-Organic Interface. *J. Phys. Chem. C* **2017**, *121*.

(45) M. A. Leitch-Devlin and D. A. Williams. Sticking Coefficients for Atoms and Molecules at the Surfaces of Interstellar Dust Grains. *Mon. Not. R. astr. Soc.* **1985**, *213*, 295–306.

(46) Tsai, H. Z.; Omrani, A. A.; Coh, S.; Oh, H.; Wickenburg, S.; Son, Y. W.; Wong, D.; Riss, A.; Jung, H. S.; Nguyen, G. D.; *et al.* Molecular Self-Assembly in a Poorly Screened Environment: F4TCNQ on Graphene/BN. *ACS Nano* **2015**, *9*, 12168–12173.
Figure captions:

Fig. 1. a) the band structure of silicon and F₄TCNQ before contact; b) the device configuration studied in this work: buried oxide/Si/F₄TCNQ. And The charge transfer is only effective in proximity of the interface.

Fig. 2: a) Device configuration for transport measurements; b) 90° zoom-in view of a) with Si device layer, heater and thermometers annotated.

Fig. 3: Surface morphology of F₄TCNQ with a) 10 μm × 10 μm and b) 2 μm × 2 μm by AFM.

Fig. 4: a) XTEM of the device by FIB lift-out, with each layer annotated; b) high-resolution TEM image of F₄TCNQ—Si interface along Si [110]. The inset shows the convergent-beam electron diffraction (CBED) pattern.

Fig. 5: Comparison of IV curves for Si and F₄TCNQ – Si device. The embedded figure is the optical image of the device partially deposited with F₄TCNQ using a shadow mask.

Fig. 6: a) Comparison of Seebeck voltage for Si and F₄TCNQ – Si devices; b) – e) resistance curves of each thermometer when heater is on/off.