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Soft-etching Copper and Silver Electrodes for Significant Device Performance Improvement towards Facile, Cost-effective Bottom-contacted Organic Field-effect Transistors

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ABSTRACT: Poor charge injection and transport at the electrode/semiconductor contacts has been so far a severe performance hurdle for bottom contact bottom gate (BCBG) organic field effect transistors (OFETs). Here, we have developed a simple, economic and effective method to improve the carrier injection efficiency and obtained the high-performance devices with low-cost and widely used source/drain (S/D) electrodes (Ag/Cu). Through the simple electrode etching process, the work function of the electrodes is more aligned with the semiconductors, which reduces the energy barrier and facilitates the charge injection. Besides, the formation of the thinned electrode edge with desirable micro/nanostructures not only leads to the enlarged contact side area beneficial for the carrier injection but also is in favor of the molecular self-organization for the continuous crystal growth at the contact/active channel interface, which is better for the charge injection and transport. These effects give rise to the great reduction of contact resistance and the amazing improvement of the low-cost bottom-contact configuration OFETs performance.

1. INTRODUCTION

Bottom-contact (BC) is a feasible device geometry for mass production of organic field-effect transistors (OFETs), while their device performance is always inferior comparing to top-contact (TC) devices due to the high contact resistance (R_c).¹⁻¹² As R_c mainly depends on the charge injection and transport, thus choosing energy-matched electrodes to minimize the charge injection barrier is a good choice.⁶⁻¹³ Up to now, gold (Au) is still be the primary electrode candidate, for the merits of excellent conductivity, good stability and aligned energy level with most p-type semiconductors, however, Au is limited for the practical application due to the high cost. Nevertheless, cheap metals (such as Ag and Cu) yet always possess the unmatched energy levels with most of p-type organic semiconductors for their low work functions, which also impede the fabrication of high performance BC-OFETs.¹⁴⁻¹⁶ In order to fulfill the band alignment at the semiconductor/electrode contacts, many efforts such as judicious electrode modification, finely semiconductor doping and others have been devoted to improve the charge injection efficiency.¹⁷⁻²⁶ However, besides the energy offset, other factors, such as the injection area and the interface molecular packing can also greatly influence R_c .²⁷⁻³³ The enlarged contact area with the rough boundary by the formation of Cu-TCNQ has already been proven to effectively facilitate the charge injection.³² The ordered molecular packing at the contacts can benefit the formation of continuous interface and guarantee the efficient charge injection and transport, which even determines the device performance.²⁷⁻³⁰ Despite of these efforts, most of studies focus on a particular aspects and the procedures always exhibit expensive, time-consuming and inconvenient. Therefore, a novel, facile and universal approach to optimize the charge injection and transport efficiency at the interface between organic semiconductor and cheap source/drain electrodes still remains to be developed.

Here, we report a simple, powerful and facile method to achieve high performance BC-OFETs by soft-etching low-cost metal electrodes (Ag & Cu). We introduce a simple electrode etching process with 2:3,5:6-bis(1,1-dicyanoethylene-2,2-dithiolate)-quinone (BDQ, **Figure 1**) and dilute nitric acid (HNO_3 , **Figure 1**), i.e., one etchant is organic and another is inorganic, which can react with Cu/Ag electrodes to form soluble complexes and afford desirable micro/nanostructures at the edge of metal electrodes (**Figure 2**). Devices

based on the soft-etched bottom-contact electrodes exhibit significant performance enhancement either for p-type (pentacene, CuPc and TIPS pentacene) or n-type (F_{16} -CuPc) semiconductors, which is comparable or even better than the corresponding devices with top-contact gold electrode. This approach, which avoids the insertion of buffer layer between the semiconductor/electrode interface, provides a simple and effective way to construct high performance, low-cost BC-OFETs.

2. RESULTS AND DISCUSSION

BDQ is taken as the electrode etchant for presentation firstly, as it could react with low-cost metals (Ag and Cu) to form the metal complex, which has better solubility than BDQ itself and so that the complex would dissolve in the solution once the reaction completed (**Figure S1**).^{34, 35} **Figure 2a** and **2b** depict the scanning electron microscopy (SEM) images of etched Ag and Cu electrodes by BDQ and their corresponding unetched electrodes for comparison, respectively. After the etching process, the metal atoms of the electrodes especially along the edge were vanished and the desirable micro/nanostructures were generated, that is, on and near the contacts edge, an obvious morphology and grain size change exhibited, where appeared many holes and semidetached metalics and the metal grain size became larger than the unprocessed ones, which resulted an extension contacting line and a rough edge and therefore an enlarged contact area.

Based on these etched Ag (or Cu) bottom-contact S/D electrodes, a series of pentacene OFETs are fabricated, and we also prepare the bare (unetched) Ag (or Cu) bottom-contact S/D electrodes and Au top-contact S/D electrodes based devices for comparison. The etched electrodes with micro/nanostructure indeed have a dramatic influence on the device performance (**Figure S2** and **Figure 2**). Here as the electrodes etching time had a fairly limited impact on the device performance (**Figure S2**), we etched Ag (or Cu) electrodes with BDQ for around 2 minutes. As shown in **Figure 2c**, the saturation current of BC devices with etched Ag electrodes was up to $-122\ \mu\text{A}$ at a gate voltage of $-85\ \text{V}$, which was almost 14 times larger than that using unetched (bare) Ag S/D electrodes ($-9\ \mu\text{A}$), indicating the dramatically improved electrode/semiconductor contact.³² Their field-effect performance exhibited a striking improvement with the

average mobility ($1.33 \text{ cm}^2/\text{Vs}$) nearly one order of magnitude higher than that of BC devices with bare Ag ($0.15 \text{ cm}^2/\text{Vs}$) electrodes, which was even better than that with top-contact Au electrodes ($1.28 \text{ cm}^2/\text{Vs}$). The on/off ratio also got a tremendous enhancement, as high as $10^7 \sim 10^8$. Similar phenomena are also observed for devices with Cu electrodes as shown in **Figure 2d**. The BDQ-etched Cu electrodes based devices exhibited a dramatic performance improvement, that the maximum mobility ($1.22 \text{ cm}^2/\text{Vs}$) was nearly 7 times larger than that with bare Cu BC electrodes ($0.18 \text{ cm}^2/\text{Vs}$), and much better than the TC devices with Au electrodes ($0.88 \text{ cm}^2/\text{Vs}$). Moreover, the soft-etched process can as well greatly reduce the threshold voltage as it decreased from $\sim 55 \text{ V}$ for bare based devices to $\sim 15 \text{ V}$ for etched based ones. The experiments have been repeated several times and the performance improvement was obvious for each time either on octadecyltrichlorosilane (OTS) modified SiO_2/Si substrates or bare SiO_2/Si substrates. Here we fabricated devices with Cu S/D electrodes on bare substrates due to the poor adhesion of copper film on the OTS modified substrates during the etching process. All detailed device performance (on/off ratio, mobility and threshold voltage) with different S/D electrodes are summarized in **Table 1**. It's worth to note that our result is one of best in BC OFET performance reported (**Table S1**).

Here, to exclude the etching process effect on the active channel, we prepare Au top-contact devices with the substrates treated by the etchants (**Figure S3**), and the results showed that the etchants have little impact on the pentacene performance in the channel. Therefore, considering the almost identical active channels in every set of devices, the great enhancement of OFETs performance based on etched electrodes might largely stem from the improvement of the charge carrier injection efficiency. Given this, the contact resistance (R_c) of various electrodes was calculated (**Figure S4 and Table S2**),^{36, 37} and as expected, the R_c of devices with etched Ag electrodes ($0.0395 \text{ M}\Omega$) was reduced by nearly 2 orders of magnitude than the bare ones ($3.24 \text{ M}\Omega$). Similarly, the great reduction of the R_c was as well observed for the etched Cu electrodes. In general, for the BCBG geometry devices, the contact resistance is mainly determined by three factors, the energy barrier (ϕ_b) between the work function (WF) of electrodes and the semiconductor energy levels, the carrier

injection area (S) and the electrode/semiconductor contact condition.^{6-12, 17, 32} Here, we would elaborate on them in the next section.

As well known, the energy barrier (ϕ_b) definitely plays a pivotal effect on the contact resistance. Due to the highest occupied molecular orbital (HOMO) of pentacene of ~ 4.9 eV, the improved WFs of Ag or Cu electrodes to energetically compatible with HOMO of pentacene are obviously in demand. From the calculated WFs in **Figure 3a** and **3d** by ultraviolet photoelectron spectroscopy (UPS) analysis,³⁸ we found that the etching process could make their WFs increased, with 0.45 eV higher than that of bare (unetched) Ag ones (4.41 eV) for BDQ-etched Ag electrodes (4.86 eV), and 0.28 eV higher than that of bare (unetched) Cu ones (4.34 eV) for BDQ-etched Cu electrodes (4.62 eV). To clarify the origin of the increased WFs, we carefully characterize the electrodes surface with X-ray photoelectron spectroscopy (XPS) and X-ray Auger electron spectroscopy (XAES) as illustrated in **Figure 3**.³⁸ Here the fresh Ag and Cu surfaces (Ag-Ar⁺ and Cu-Ar⁺) by *in-situ* Argon ion beam etching to remove surface impurities and the electrodes with AgO_x and CuO_x layer from O₂ plasma treatment on the evaporated electrodes are also prepared for comparison. From the XPS (**Figure 3b** and **3e**) and XAES (**Figure 3c** and **3f**) results, neither the binding energy peaks nor the kinetic energy peaks of the BDQ-etched Ag or Cu electrodes exhibited apparent shifts comparing with the bare (unetched) ones. Specifically, no recognizable or very weak new Ag oxide component is brought about on the BDQ-etched Ag films, as almost the same position and same content of Ag 3d XPS and Ag *MNV* XAES peaks is observed compared with the bare (unetched) and the Argon ion beam etched ones (Ag-Ar⁺).³⁹ Nevertheless, the Cu films seems to be much more complicated as Cu is very prone to be oxidized even in the vacuum condition of 10⁻³ Pa.⁴⁰ We analyze them through Cu *LMM* Auger spectra (**Figure 3f**). Comparing to the Cu-Ar⁺ (kinetic energy of 918.4 eV refer to metallic Cu, Cu(0)), the proportion of 916.2 eV peak (refer to oxidation state of Cu, Cu(I)) intensity showed obvious increase for the bare (unetched) and the BDQ-etched Cu electrodes, indicating the already formation of oxide state of Cu even on the bare Cu surface.⁴¹ Given this, the increased WF of bare (unetched) Cu electrode (4.34 eV) compared to Cu-Ar⁺ (4.24 eV) can be partly ascribed to the formation of the surface native oxide layer. Moreover, the proportion of Cu(I) for

BDQ etched Cu is obviously higher than that for the bare (unetched) one, leading to the higher WF of BDQ etched Cu. But surprisingly, the detected WF of bare Ag (unetched) electrodes (4.41 eV) was also higher than its corresponding Ag-Ar⁺ (4.22eV), which is probably due to the physical or chemical adsorption of contamination from ambient exposure as the existence of oxygen element from the XPS result (**Figure S5**).⁴² In addition, we speculate that the further increased WFs of the BDQ-etched either Ag or Cu electrodes comparing with their correspondingly unetched ones might derive from the effect of the polarity solution and the possible BDQ residues or the weak BDQ chemisorption onto the electrode surfaces, where the generated micro/nanostructures can effectively increase the contact area and reactivity with the substance in the ambient, in other words, facilitate the adsorption and lead to the formation of the interface dipole layer.^{17, 22-23} This can be partly verified through the obviously enhanced intensity of O 1s peak for the BDQ-etched electrodes compared with their bare ones (**Figure S5**). Meanwhile, compared with the totally generated AgO_x and CuO_x layers (after O₂ plasma treatment), the BDQ-etched electrodes exhibited a less oxidized or intermediated state, which makes this soft-etching method owns superior attractions than the traditional metal oxide layer modification method, as it not only aims to align the energy level with the semiconductors to decrease the energy barrier for the efficient charge injection but also maintains its own fine charge carrier transport interface. Specifically, as well known, although electrodes with the O₂ plasma treated oxidization layer owns the more energetically compatible WF, the oxide layer yet hinders the efficient charge transport at the interface for the low conductivity, which might have a neutral or even negative effect in developing device performance as confirmed in **Figure S6**, where the mobility increased almost twice for the soft self-oxidized Ag electrodes (stored in ambient for 5 days, with ultrathin metal oxide) based devices (0.24 cm²/Vs) but instantly decreased nearly an order of magnitude for that with total oxidized layer (by O₂ plasma treatment) Ag electrodes (0.022 cm²/Vs).

As the hole injection behavior is significantly dependent on the real hole injection barrier, rather than simple difference between WF of an electrode and HOMO of a semiconductor, we have checked the hole injection barrier formed at the interface between pentacene and the electrodes investigated here. **Figure S7**

showed the UPS spectra of HOMO region of 4 nm pentacene on different electrodes. The measured hole injection barrier, which is directly derived by linear extrapolation of the HOMO leading edge of the HOMO peak, decreased from 0.42 eV to 0.34 eV for the BDQ etched Ag electrode and from 0.47 eV to 0.37 eV for the BDQ etched Cu electrode, respectively. Apparently, the increased work function seems to be not sufficient enough to explain such largely decreased contact resistance. As analysis in supporting information (**Formula 7**), with the constant V_c and T , despite of the undisputedly vital function of ϕ_b in reducing the contact resistance, the effect of the enlargement of contact area (S) cannot be ignored as well. Especially for the bottom contact configuration, as the mobile charges are always suggested to be injected from the edges of the electrodes, the function of the contact area appears to be more critical.^{7-9, 32} From the SEM images in **Figure 2**, the etching process apparently lead to an impressive enlarged contact side area with micro/nanostructures at the electrodes edge, which undoubtedly can efficiently facilitate the carrier injection, namely, at a certain voltage many more charge carriers can inject into the conducting channel.¹⁸ Therefore, it can be concluded that the enlarged contact area aroused by the micro/nanostructures at the boundary is responsible for the further reduction of the contact resistance and the improvement of OFETs properties. Moreover, compared with devices aforementioned (contact length: 200 μm , **Table 1**), the higher mobility of 2.75 cm^2/Vs can be obtained for BDQ-etched Ag BC electrodes based devices with the longer contact length (500 μm), while the performance of devices with unetched Ag BC electrodes (0.24 cm^2/Vs) and Au TC (1.50 cm^2/Vs) electrodes just exhibit a slightly higher, which in turn confirms the importance of the contact edge (**Figure S8** and **Table S3**). Actually, the effect of this method on the enlargement of contact area is evidently more efficient than the artificial rough edge for its finer micro/nanostructures as well as its simplicity, convenience and efficiency.

Besides the enlarged contact area caused by the etching process, it can also give rise to the gradually thinned metal region on/near the channel as the reactivity of the metal edges and corners is much greater than the flat middle region. As well known, the thicker contacts can significantly disrupt the molecular self-organization, causing disordered molecular packing in the vicinity of the contacts. Instead, the thin contacts

can alleviate this molecular disorder and be more favorable for the continuous crystal growth, but thin films indicate the poor conductivity and the small contact side area, which could be the limitation for the charge transport.⁴³ However, the etched electrodes in this article can well ease this conflict as they not only own the thin film edges with enlarged contact area but also retain the good conductivity. The thinned metal region can efficiently improve the pentacene growth at the contacts as seen from AFM analysis in **Figure 4**.⁴⁴ Compared with the distinct pentacene grain size change at the electrode/channel interface for the bare metals (Ag/Cu, **Figure 4a** and **c**), the contact condition for BDQ-etched electrodes improved a lot (**Figure 4b** and **d**), with the pentacene grain size at the electrodes boundary enlarged approximately from 100nm to 400nm for Ag electrodes and from 200nm to 400 nm for Cu electrodes, respectively, which brought about a homogeneous morphology to improve the interface connectivity and guarantee an efficient carrier injection/transport. This continuous crystal growth is definitely responsible for the acquisition of the dramatic performance enhancement.²⁷⁻³⁰ Moreover, we also compare the pentacene crystalline structure change on the electrode surface before and after etching process by X-ray diffraction analysis (**Figure S9**), but unfortunately, the results don't show the significant change. So we'd like to use the more convincing techniques and the relevant work is further going.

In addition, to verify this soft etching electrode method independent of the kinds of etchant, we also process the Ag and Cu electrodes with dilute HNO₃ (3.0% ~ 4.0%), which likewise leads to the formation of micro/nanostructures at the electrode/semiconductor contact (**Figure 5**). In fact, similar conclusions are also found for the HNO₃-etched ones. As XPS, XAES and UPS analysis shown in **Figure 3**, the HNO₃ etched electrodes surface properties as well as the work functions were almost identical with the BDQ-etched ones for Ag of 4.82 eV and Cu of 4.55 eV, respectively. The UPS for the measurement of the hole injection barrier of pentacene on HNO₃-etched Ag or Cu electrode in **Figure S7** also confirms the improved hole injection property. Furthermore, the performance of pentacene-based devices also exhibits a dramatic improvement after electrodes etched by HNO₃. The maximum mobility of device with etched Ag electrode (1.82cm²/Vs) increased nearly seven times than bare ones (0.27cm²/Vs), and the corresponding I_{on}/I_{off} increased one or two

orders of magnitude. The phenomena are as well applied to Cu electrodes, and the maximum mobility of OFETs with etched Cu electrodes ($1.04 \text{ cm}^2/\text{Vs}$) exhibited nearly one order of magnitude higher than unetched ones ($0.18 \text{ cm}^2/\text{Vs}$). Their performance was even comparable to that of devices with top-contact Au electrodes. **Figure 5** depicts the typical output and transfer characteristics of HNO_3 -etched electrodes based devices compared to bare ones. The great enhancement of the performance further confirms the credibility of our explanation.

To further confirm the universal applicability of this electrodes etched method on other semiconductors, we also fabricate the BC OFETs based on another three benchmark semiconductors: p-type copper phthalocyanine (CuPc), 6,13-Bis(triisopropylsilylethynyl) pentacene (TIPS pentacene) and n-type fluorinated copper phthalocyanine (F_{16}CuPc). The detailed characteristics are summarized in **Table 1**. All the devices are fabricated at the room substrate temperature and the average results are obtained from 5-10 devices. It's excited that the performance is improved distinctly for devices with etched electrodes regardless of which kind of semiconductor based or etchant used (**Figure S10**). For CuPc based devices, for example, the average mobility with both BDQ and HNO_3 etched Ag electrodes was increased nearly one order of magnitude in contrast to that of bare ones. This is due to the reduced energy barrier for the enhanced charge injection as well as the thinned contacts region with large contact area for the better crystal growth and charge transport. The F_{16}CuPc based devices with etched Ag/Cu electrodes also exhibited a greater performance improvement. Besides the vacuum-evaporated semiconductors, the soft-etched electrodes are also applicable for the solution-processed semiconductors, as devices based on the solution-processed TIPS pentacene with etched Ag/Cu electrodes also exhibited the great performance enhancement, indicating its potential and widely use in the future electronic industry.

All above observations illustrate that the etched BC low-cost electrodes exhibit superior performance over the corresponding unetched ones and even the traditional TC Au electrodes in OFETs based on conventional p- and n-type organic semiconductors fabricated in the same condition. And it further proves that other factors such as contact area, contact condition apart from the energy barrier also play an important role in

promoting the charge injection. This method displays its own advantages for its: 1) providing a new train of thought to improve the electrode/semiconductor interface, 2) economic and convenient solution process for industrial application, 3) outstanding performance comparable to TC devices, and 4) excellent applicability to various semiconductors. All these advantages indicate that this method has huge potential in the development of bottom-contact organic field-effect transistors and might render it in commercial applications.

3. CONCLUSION

In summary, we have developed a simple, economic and effective method to improve the properties of bottom-contact devices based on low-cost and widely used electrodes (Ag/Cu). Electrode etching process brings about the reduction of contact resistance by the aligned work function and the formation of the thinned electrode edge with desirable micro/nanostructures, which causes an efficient energy barrier reduction and enlarged contact side area better for charge injection as well as the continuous crystal growth better for the charge transport at the contact/semiconductor interface. Our method could open a new window to develop high-performance low-cost BC-OFETs.

4. EXPERIMENTAL SECTION

Materials: 2:3,5:6-bis(1,1-dicyanoethylene-2,2-dithiolate)-quinone (BDQ) was used as received from Zhang Qichun's group.⁴⁵ Nitric Acid (HNO₃) (AR) was used as purchased. Pentacene and copper phthalocyanine (CuPc) were purchased from Aldrich and purified by sublimation method for three times. Fluorinated copper phthalocyanine (F₁₆CuPc) were purchased from Aldrich and purified by sublimation method for once. 6,13-Bis(triisopropylsilylethynyl) pentacene (TIPS pentacene) was purchased from Aldrich.

Devices Fabrication: The BDQ etchant was obtained by ultrasonically dissolving BDQ in acetonitrile (HPLC) to form a saturated solution. HNO₃ etchant was obtained by adding deionized water to concentrated nitric acid (65% ~ 68 %) to dilute 16-22 times. OTFTs were fabricated on a highly n-doped silicon wafer with a 300nm thermally oxidized SiO₂ dielectric layer ($C_i = 10 \text{ nF/cm}^2$), where the silicon served as the gate electrode and oxide layer was the insulator. Before patterning the Ag S/D electrodes, surface treatment of the

SiO₂ substrate with octadecyltrichlorosilane (OTS) was performed, yet the Cu S/D electrodes were directly patterned on the bare SiO₂ substrates without OTS-treatment, as the Cu electrodes were liable to peel off from the OTS-modified substrates in etching process for their surface tension difference. The patterned Ag (40 nm) and Cu (40nm) S/D electrodes were thermally evaporated at a rate of 0.5 Å/s with a base pressure of 10⁻⁶ mbar through shadow masks. The channel width was obtained as 500 μm and channel length were 200, 100, 50, 30 μm for the interdigital masks, respectively, as well as the channel width was 200 μm and channel length was 25 μm for the copper grid mask. Thereafter the substrates with freshly patterned Ag and Cu electrodes were immersed in BDQ or HNO₃ etchant for seconds to minutes, then rinsed with acetonitrile or ethanol, respectively, and finally dried with N₂ stream. The substrates with etched electrodes were annealed at 60 °C in a vacuum oven for 0.5 h to eliminate the residual solvent. After that, 50 nm semiconductor films (pentacene, CuPc and F₁₆CuPc) were thermally deposited on the substrates at a rate of 0.1-0.5 Å/s with a base pressure about 10⁻⁶ mbar. ~50 nm TIPS pentacene films were fabricated by spin-coating the solution in CHCl₃ (10 mg/mL) at a rate of 2000 rpm for 30s and then thermally annealed for ~ 30 min in a vacuum chamber at a temperature of 80 °C. Top-contact OFETs were also fabricated for comparison, all the conditions were the same except 20nm gold deposition after the semiconductor deposition. All the substrates were kept at room temperature ($T_s = 20$ °C) during the deposition process.

Measurements: The electrical measurements of OFETs were characterized using a Keithley 4200 SCS semiconductor parameter analyzer and a Micromanipulator probe station in the ambient environment at room temperature. AFM experiments were performed on a Nanoscopy IIIa (USA) in a tapping mode. SEM images were conducted with a Hitachi S-4300 SE (Japan). X-ray photoelectron spectroscopy (XPS) and X-ray Auger electron spectroscopy (XAES) experiments were performed on a KRATOS Axis Ultra DLD spectrometer equipped with a monochromatized Al K α X-ray source (1486.6 eV) and a hemispherical analyzer (base pressure < 2 × 10⁻⁹ Torr). The pass energy was operated at 20 eV with take-off angles of 90°. Ultraviolet photoelectron spectroscopy (UPS) experiments were conducted using a non-monochromatized He I (21.22 eV) gas discharge lamp radiation at detection angles perpendicular to the sample surfaces with a total

instrumental energy resolution of 0.1 eV (base pressure $< 3 \times 10^{-8}$ Torr during UPS measurements). UV-*vis* absorption was conducted on a JASCO V-570 UV-*vis* spectrometer in acetonitrile solution. Raman spectroscopy (RAMAN) was recorded on Renishaw Invia plus and Fourier transform infrared (FTIR) spectra were conducted on TENSOR 27.

Figure 1. Schematic illustration of the electrode (Ag or Cu) etching process by etchants (BDQ or HNO_3) for the fabrication of OFETs based on various semiconductors (pentacene, CuPc, F_{16}CuPc or TIPS pentacene). (a) Dropping etchants onto the SiO_2 substrate with the bottom patterned Ag or Cu source-drain electrodes. (b) The etched source-drain electrode. (c) Fabricating the bottom-contact bottom-gate (BCBG) OFETs based on the etched electrodes. (d) The diagram details of the etched electrodes.

Figure 2. SEM images of (a) bare (unetched) and BDQ etched Ag electrodes and (b) bare (unetched) and BDQ etched Cu electrodes, respectively (the inner bar scale: 1 μm); Output and transfer characteristics of the OFETs based on pentacene with (c) various Ag electrodes and (d) various Cu electrodes: black line, red line, and blue line refer to with BDQ etched BC electrodes, bare (unetched) BC electrodes and Au TC electrodes, respectively. (a, c on the OTS modified substrates and b, d on the bare substrates because of the poor adhesion of copper film on the OTS modified substrates during the etching process)

Figure 3. (a) UPS, (b) Ag 3d XPS spectra and (c) Ag *MNN* Auger spectra obtained from the various Ag electrodes; (d) UPS, (e) Cu 2p XPS spectra and (f) Cu *LMM* Auger spectra obtained from the various Cu electrodes.

Figure 4. AFM images of pentacene deposited on the surface of (a) bare and (b) BDQ etched Ag S/D electrodes, (c) bare and (d) BDQ etched Cu S/D electrodes (inset: the corresponding amplitude images; the inner bar scale: 1 μm)

Figure 5. SEM images of etched (a) Ag and (b) Cu electrodes by dilute HNO₃, respectively (the inner bar scale: 1 μ m); Transfer characteristics of the pentacene OFETs with (c) various Ag BC electrodes and (d) various Cu BC electrodes (black line:HNO₃-etched, red line: bare); Output characteristics of the pentacene based BC devices with HNO₃ etched (e) Ag S/D electrodes and (f) Cu S/D electrodes, respectively.

Table 1. Summary of properties of OFETs based on pentacene, CuPc, F₁₆CuPc and TIPS pentacene with various S/D electrodes, respectively (channel width: 200 μm , channel length: 25 μm).

Semiconductor	Electrode ^{a)}	Properties			Substrate ^{b)}
		Mobility [cm^2/Vs]	$I_{\text{on}}/I_{\text{off}}$	V_t [V]	
Pentacene	Ag	0.15 ± 0.06	$10^6 \sim 10^7$	-4.1~-7.7	OTS
	Ag-BDQ	1.33 ± 0.35	$10^7 \sim 10^8$	1.1~7.0	
	Ag-HNO ₃	1.65 ± 0.15	10^8	-11.0~-13.1	
	Au	1.28 ± 0.03	10^8	-10.4~-11.9	
	Cu	0.09 ± 0.06	$10^5 \sim 10^6$	-41.8~-55.2	Bare
	Cu-BDQ	0.99 ± 0.16	$10^7 \sim 10^8$	-1.9~-15.0	
	Cu-HNO ₃	0.95 ± 0.06	10^8	-14.3~-17.4	
	Au	0.69 ± 0.13	$10^7 \sim 10^8$	-16.7~-17.9	
CuPc	Ag	$(0.34 \pm 0.10) \times 10^{-2}$	10^2	0.4~18.3	OTS
	Ag-BDQ	$(3.32 \pm 0.66) \times 10^{-2}$	$10^3 \sim 10^4$	-2.2~3.4	
	Ag-HNO ₃	$(2.76 \pm 0.34) \times 10^{-2}$	$10^3 \sim 10^4$	1.4~4.1	
	Au	$(5.59 \pm 1.64) \times 10^{-2}$	$10^4 \sim 10^5$	-2.5~0.03	
	Cu	$(0.20 \pm 0.13) \times 10^{-2}$	10^2	9.7~44.3	Bare
	Cu-BDQ	$(1.01 \pm 0.09) \times 10^{-2}$	$10^2 \sim 10^3$	-9.7~2.9	
	Cu-HNO ₃	$(1.26 \pm 0.22) \times 10^{-2}$	$10^3 \sim 10^4$	-15.4~0.3	
	Au	$(0.67 \pm 0.05) \times 10^{-2}$	$10^3 \sim 10^4$	16.9~24.4	
F ₁₆ CuPc	Ag	$(0.39 \pm 0.19) \times 10^{-3}$	$10^3 \sim 10^4$	29.1~47.2	OTS
	Ag-BDQ	$(5.48 \pm 0.57) \times 10^{-3}$	$10^4 \sim 10^5$	5.2~16.7	
	Ag-HNO ₃	$(5.56 \pm 0.64) \times 10^{-3}$	$10^4 \sim 10^5$	12.2~24.8	
	Au	$(5.34 \pm 0.79) \times 10^{-3}$	10^4	3.2~11.3	
	Cu	$(0.53 \pm 0.28) \times 10^{-4}$	$10^2 \sim 10^3$	-3.70~4.01	Bare
	Cu-BDQ	$(7.44 \pm 1.60) \times 10^{-4}$	$10^3 \sim 10^4$	-4.38~7.48	
	Cu-HNO ₃	$(16.3 \pm 1.23) \times 10^{-4}$	$10^3 \sim 10^4$	-5.97~-15.3	
	Au	$(25.8 \pm 2.06) \times 10^{-4}$	$10^3 \sim 10^4$	-13.2~4.81	
TIPS Pentacene	Ag	$(0.74 \pm 0.2) \times 10^{-3}$	$10^3 \sim 10^4$	-33.3~-35.4	OTS
	Ag-BDQ	$(7.90 \pm 0.5) \times 10^{-3}$	$10^4 \sim 10^5$	-14.6~-17.5	
	Ag-HNO ₃	$(3.12 \pm 0.6) \times 10^{-3}$	$10^4 \sim 10^5$	-26.0~-35.3	
	Cu	$(0.11 \pm 0.02) \times 10^{-4}$	10^2	-16.5~-22.9	Bare
	Cu-BDQ	$(1.33 \pm 0.2) \times 10^{-4}$	$10^3 \sim 10^4$	-26.2~-33.1	
	Cu-HNO ₃	$(6.52 \pm 2.0) \times 10^{-4}$	10^3	-31.9~-32.9	

^{a)}The various Ag and Cu S/D electrodes based devices were bottom contact bottom gate geometry, while the Au S/D electrodes based devices were top contact bottom gate geometry. ^{b)}Devices with Cu S/D electrodes fabricated on bare substrates was due to the poor adhesion of copper film on the OTS modified substrates during the etching process.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications websites at <http://pubs.acs.org>. Further discussion on the electrodes etching process. The calculation of OFET performance and the contact resistance. The addition of the performance comparison and analysis as well as the XPS and UPS analysis.

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Notes

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Table of Contents Graphic

Supporting Information

Soft-etching Copper and Silver Electrodes for Significant Device Performance Improvement towards Facile, Cost-effective Bottom-contacted Organic Field-effect Transistors

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1. The analysis of the reaction between BDQ and Ag/Cu

Figure S1. (a) UV-*vis*, (b) IR and (c) Raman of reaction production of Ag/Cu with BDQ.

The low-cost metal (Ag or Cu) was dissolved in the BDQ saturated solution with the apparent solution color change (**Figure S1a inner**). The analysis of UV-*vis*, IR, and Raman clearly proved the reaction of BDQ with the metals. From the UV-*vis* spectrum, the main peak showed the obvious red-shift after the completion of the reaction. And the peaks shift in IR and Raman further confirmed the realization of this reaction as well. In short, the reaction between BDQ and the low-cost metal (Ag or Cu) indeed happened, but the exact mechanism was still unclear and remained to be investigated and confirmed.

2. The effect of electrodes etching time on the performance of pentacene based devices.

Figure S2. The pentacene based OFETs performance (mobility, black square; threshold voltage, red circle) change with the etching time of bottom-contact (a) BDQ etched Ag electrodes, (b) HNO_3 etched Ag electrodes and (c) BDQ etched Cu electrodes. For the HNO_3 etched Cu electrodes, the etching time was merely one second as the copper reacts readily even with the dilute HNO_3 solution. The Ag

electrodes were patterned on OTS-modified SiO₂/Si substrates and the corresponding mobility of Au top-contact based devices was $0.48 \pm 0.04 \text{ cm}^2/\text{Vs}$. The Cu electrodes were patterned on bare SiO₂/Si substrates and the corresponding mobility of Au top-contact based devices was $0.30 \pm 0.02 \text{ cm}^2/\text{Vs}$. The inferior performance here relative to that listed in the manuscript is due to the lower purity pentacene.

From the diagram of the effect of electrodes etching time on the pentacene based devices performance, it is concluded that the etching process indeed can greatly improve the device properties as the mobility increased sharply, the standard deviation became smaller and threshold voltage decreased when electrodes etched by BDQ or HNO₃ either for Ag or Cu electrodes. With the etching time, the performance improvement was still significant despite with a little attenuation which might be due to the slight W/L ratio increment and electrodes properties decay. Besides, the results also showed that the etching time can be over a wide range from seconds to minutes, that's because the etchants we chose were mild and most importantly, the etching process occurred mainly at the electrodes edge while did little impact on the electrodes body, so that the contacts can own both the thinned edge region with enlarged contact side area and the nice electrodes properties. The best etching time roughly ranged from 30 seconds to 3 minutes.

3. The calculation of the performance of the OFETs

The mobilities were extracted from the typical transfer characteristics with the widely used devices equation for the saturation regime as follows:

$$I_{D,sat} = \mu C_i (W/2L)(V_G - V_T)^2 \quad (1)$$

where W and L were the channel width and channel length, respectively. μ was the field-effect mobility, C_i the gate dielectric capacitance per unit area, V_G the gate voltage V_T the threshold voltage and $I_{D,sat}$ was the saturated drain current.

Table S1. The comparison of pentacene based OFET properties with various modified electrodes reported to the results of this report.

Dielectric	Mobility μ (cm ² /Vs)	I_{on}/I_{off}	Electrode	$T_{substrate}$ (°C)	Configuration	Reference
SiO ₂	0.31	10 ⁷	Cu-TCNQ	RT	BCBG	1
SiO ₂	0.47-0.53	-	Ag-graphene	RT	BCBG	2
	0.47-0.53	-	Cu-graphene			
SiO ₂ /OTS	0.18	10 ⁶	Ag-TCNQ	RT	BCBG	3
	0.1	10 ⁶	Cu-TCNQ	RT	BCBG	
Teflon	0.28	-	Printed Ag	RT	BCBG	4
SiO ₂	0.21	10 ³	Ag-HDT/FDT	RT	BCBG	5
HfO ₂ /OPA	0.8	10 ⁷	Ag/OPA	60	BCBG	6
HfO ₂ /DDPA	0.8	10 ⁶	Ag/DDPA	60	BCBG	
HfO ₂ /ODPA	0.16	10 ⁴	Ag/ODPA	60	BCBG	
SiO ₂	0.13	-	Au/HRG	RT	BCBG	7
SiO ₂	0.01	10 ³	Cu/Ti	70	BCBG	8
SiO ₂ /OTS	2.75	10 ⁸	Ag-BDQ	RT	BCBG	This report
	1.82	10 ⁸	Ag-HNO ₃	RT	BCBG	
SiO ₂	1.22	10 ⁸	Ag-BDQ	RT	BCBG	
	1.04	10 ⁸	Ag-HNO ₃	RT	BCBG

Figure S3. The mobility of pentacene based Au top-contact OFETs on (a) untreated, BDQ-treated and HNO_3 -treated SiO_2/Si substrates and (b) untreated, BDQ-treated and HNO_3 -treated OTS-modified SiO_2/Si substrates.

4. The calculation of the contact resistance of OFETs based on pentacene semiconductor

We estimated their contact resistance (R_c) using the transfer line method (TLM) in the linear region⁹.

When the space charge limited current (SCLC) effect is neglected, the R_{ON} , namely the overall device resistance, in the linear regime, can be calculated by the following formula ($V_{SD} \ll V_G$):

$$R_{ON} = \left. \frac{\partial V_{SD}}{\partial I_{SD}} \right|_{V_{SD} \rightarrow 0}^{V_{GS}} = R_{ch} + R_c = R_{sh} \frac{L}{W} + R_c \quad (2)$$

$$R_{sh} = \frac{1}{\mu_c C_i (V_{GS} - V_{Ti})} \quad (3)$$

Where R_{ch} , R_c , and R_{sh} are the sum of channel resistance, total contact resistance, and sheet channel resistance, respectively. μ_c , C_i , V_{GS} and V_{Ti} are the intrinsic device mobility, the gate dielectric capacitance, the gate voltage and the intrinsic threshold voltage, respectively. When kept channel width (W) as a constant, the total contact resistance R_c can be deduced from Eqs (2) and (3) by plotting R_{ON} as a function with channel length, L . From the plot of the total resistance versus various channel length of devices (**Figure S4**), we can calculated their contact resistance (**Table S2**).

Figure S4. Relationship between the ON resistance and channel length at the gate voltage of -20 V for pentacene devices based on bottom-contact (a) BDQ-etched Ag electrodes, (b) bare Ag electrodes, (c) BDQ-etched Cu electrodes and (d) bare Cu electrodes with different channel length (200 um, 100um, 50um, 30um).

Table S2. The contact resistance of the pentacene based OFETs with the bare and BDQ-etched Ag and Cu bottom-contact electrodes calculated from the TLM method.

	Ag	Ag-BDQ	Cu	Cu-BDQ
Contact Resistance (MΩ)	3.24	0.0395	866	24.9

5. The factors on the contact resistance.

For the Schottky contact, the relationship of voltage and the carrier injection current density, J , can be expressed as follows:^[1]

$$J = J_0[\exp(qV_c/kT) - 1] \quad (4)$$

$$J_0 = A^*T^2\exp(-q\phi_b/kT) \quad (5)$$

Where J_0 referred to the current density without electric field, V_c the bias voltage of electrode/semiconductor contact, q the electric charge of one electron, k the Boltzmann constant, ϕ_b the energy barrier between the work function (WF) of electrodes and the semiconductor energy levels and T the temperature.

$$I = J^*S \quad (6)$$

$$R = \frac{\partial V}{\partial I} = \frac{\partial V}{\partial (J * S)} = \frac{\partial V}{\partial J} * \frac{1}{S} \quad (7)$$

From the formula (7), it demonstrated that, with the constant bias voltage, the contact resistance (R_c) was related to the energy barrier (ϕ_b) and the carrier injection area (S). Besides, the contact condition, i.e., the crystal growth of semiconductor on the contact, also has an effect on the contact resistance by influencing the charge transport.

Figure S5. The comparison of O1s XPS spectra of (a) various Ag and (b) various Cu electrodes.

Figure S6. The performance comparison of pentacene based OFETs with different degree oxidized-Ag electrodes and the etched Ag electrodes.

Figure S7. UPS spectra of the HOMO region of 4 nm pentacene on different electrodes.

Figure S8. Output characteristics of the OFETs based on pentacene with BDQ etched Ag BC electrodes (a, black line), bare Ag BC electrodes (b, red line) and Au TC electrodes (c, blue line), and their corresponding transfer characteristics (d, channel width: 500 μm , channel length: 200 μm).

Table S3. Summary of properties of pentacene based OFETs on Ag bottom-contact electrodes, BDQ modified Ag bottom-contact electrodes and Au top-contact electrodes, respectively (channel width: 500 μm , channel length: 200 μm).

Semiconductor	Electrode ^{a)}	Properties			Substrate	W/L
		Mobility [cm^2/Vs]	I_{on}/I_{off}	V_t [V]		
Pentacene	Ag	0.20 ± 0.04	$10^5 \sim 10^6$	-6.5~-11.1	OTS	17.5
	Ag-BDQ	2.10 ± 0.65	$10^7 \sim 10^8$	6.2~10.0		
	Au	1.21 ± 0.26	$10^4 \sim 10^6$	-2.2~-5.4		

6. The analysis of the pentacene crystallinity on the electrodes surface

Figure S9. $\theta/2\theta$ scans of pentacene thin films deposited on the (a) bare SiO₂ surface and various Cu electrodes surface, and (b) OTS-modified SiO₂ surface and various Ag electrodes surface.

The diffraction peaks indicate that the pentacene films deposited on the metal surface (Ag or Cu) consist of both “thin-film phase” (t, $d_{001} = 15.5$ Å) and “single-crystal phase” (s, $d_{001} = 14.5$ Å). And with the absence of diffraction peaks corresponding to the lower d spacing for the clue of the flat-on orientation, we speculate that the pentacene molecules are probably arranged on the electrodes perpendicular to the surface, which has been proven that the pentacene films on the polycrystalline metal substrate are preferentially (001) orientation (edge-on alignment) due to the no structure of long-range-ordered nucleation layer formed for the multilayer transfer.^[10, 11] However, due to the inferior long-range order of the film on the electrodes and our experimental conditions, we cannot perspicuously

give the molecular orientation change of the molecules on the electrodes before and after etching process merely by XRD measurements. Although the surface energy (**Table S4**) change before and after BDQ-etched indicates the electrodes surface change, which may induce the molecular orientation change, the unambiguous molecular orientation change still cannot be clarified. Therefore, more convincing techniques should be introduced and the relevant work is further going.

Table S4. Contact angle and surface energy of the Ag and Cu electrodes before and after soft-etched by BDQ as well as the bare and OTS-modified SiO₂ surface.

	Contact angle [°]		Surface Energy [mJ m ⁻²]		
	Water	Glycol	γ_D	γ_P	γ
Bare Ag	83.55	55.35	26.79	5.023	31.81
BDQ-etched Ag	74.25	41.65	30.00	8.136	38.14
Bare Cu	95.55	62.50	36.11	0.391	36.50
BDQ-etched Cu	82.55	55.70	24.74	6.066	30.81
OTS/SiO ₂	104.85	76.85	26.81	0.131	26.94
SiO ₂	22.05	22.90	1.748	79.98	81.73

Figure S10. Transfer characteristics of the OFETs with various electrodes based on: (a) CuPc on OTS-modified SiO₂/Si wafers; (b) CuPc on bare SiO₂/Si wafers; (c) F₁₆CuPc on OTS-modified SiO₂/Si wafers; (d) F₁₆CuPc on bare SiO₂/Si wafers; (e) TIPS pentacene on OTS-modified SiO₂/Si wafers; (f) TIPS pentacene on bare SiO₂/Si wafers.

Reference

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