Contact Resistance in Organic Field Effect Transistors: Conquering the Barrier

Matthew Waldrip, Oana D. Jurchescu, * David J. Gundlach, and Emily G. Bittle*

M. Waldrip, Prof. O. D. Jurchescu Department of Physics and Center for Functional Materials Wake Forest University Winston-Salem, NC 27109, USA E-mail: jurchescu@wfu.edu

Dr. D. J. Gundlach, Dr. E. G. Bittle Nanoscale Device Characterization Division National Institute of Standards and Technology Gaithersburg, MD 20899, USA Email: Emily.bittle@nist.gov

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Abstract

Organic semiconductors have sparked significant interest due to their inherent properties as flexible, solution processable, and chemically tunable electronic materials. In the last 10 years, the improvements in charge carrier mobility in small molecule and polymer materials has put organic semiconductors in a competitive position for incorporation in a variety of (opto-)electronic applications. One example is the organic field-effect transistor (OFET), which is the fundamental building block of many applications based on organic semiconductors. While the semiconductor performance improvements opened up the possibilities for applying organic materials as active components in fast switching electrical devices, the ability to make good electrical contact hinders further development of deployable electronics. At the same time, inefficient contacts represent serious bottlenecks in identifying new efficient electronic materials by inhibiting access to their intrinsic properties or providing misleading information. Recent work to understand the complicated relationships of contact resistance with device architecture, applied voltage, metal and dielectric interfaces, the broadened energetic states of organic semiconductors, and more has led to a steady reduction in reported contact resistance in OFETs. While impressive progress has been made, contact

resistance is still above the limits necessary to drive devices at the speed required for many active electronic components. This review covers current understanding of the origins of contact resistance and recent improvement in organic transistors, with emphasis on the electric field and geometric considerations of charge injection in field-effect transistors.

1. Introduction

With increasing interest in developing organic semiconductor devices for new applications using transparent, flexible, and bio-compatible materials, improving organic field-effect transistors (OFETs) is a topic of intense research.^[1,2] Proof-of-concept demonstrations based on OFETs include flat-panel displays, radio-frequency identification tags, active-matrix imagers, conformable sensor arrays, memories, and health monitoring systems.^[3–9] Along with designing new organic semiconductors with superior intrinsic charge transport properties, there is a stringent need to improve the device properties in order to allow organic devices to fulfill their technological perspectives. In the organic semiconductor community, contact resistance (R_c) has come under increased scrutiny as it is apparent that the final device performance is often dominated by carrier injection, rather than the transport through the semiconductor layer. Contact resistance can impact OFET development in multiple ways. First, if not accounted for, a high contact resistance may lead to inaccurate extraction of the device parameters. Second, any inaccuracies in parameter extraction can have significant consequences on material development, from generating incorrect structure-property relationships to discarding organic semiconductors whose efficient intrinsic electrical properties have been masked by inefficient contacts. Beyond OFET and semiconductor characterization, analog, low power, and high frequency applications require a greater level of device parameter control than has been obtained in typical DC, high-voltage experimental OFETs. For analog applications, e.g. integration of conditioning circuits such as local sense amps for distributed flexible sensor arrays, non-linearity of the transistor response inhibits

proper functioning and limits applicability of common models used to design circuitry. Low power device development for novel materials are hindered by the high voltage turn-on and current suppression in devices with large R_C . Considering high-frequency applications, Klauk suggested that the final performance of practical organic devices is overwhelmingly dependent on the contact resistance,^[10] to the point that improving the semiconducting material properties will not lead to the faster performance required by common applications without a significant decrease in the contact resistance. In fact, calculations suggested that for effective mobilities around 10 cm² V⁻¹ s⁻¹ and voltages around 10 V, a channel length shorter than 1 µm is necessary in order to achieve gigahertz operation, and in this regime the corner frequency is determined almost entirely by R_C . Hence, there is a critical need for in-depth studies and improvements of the injection process in OFETs to facilitate control of the contact resistance and enhancement of device properties. This makes it imperative, for the improvement of overall OFET device performance and implementation, that contact resistance evaluation and minimization become standard in OFET development.

1.1 Decades of Research on OFETs: The Impact on Contact Resistance

Contact resistance plagues all organic devices but is most prevalent in devices passing high current density, such as OFETs. (Typical current densities in OFETs are in the order of 10⁴ A/cm², compared to only 0.001 A/cm² in organic light emitting devices (OLEDs).) Controlling charge injection by minimizing contact effects in OFETs is a great challenge and remains a bottleneck for developing high performance devices, even when using high-mobility semiconductors, but the progress has been significant, especially in the past few years. A review on contact resistance in solution processed organic thin-film transistors (OTFTs) was published by Natali and Caironi in 2012,^[11] and a review of contact engineering by Liu et al. in 2015.^[12] In this review, we focus on the recent literature on charge carrier injection and contact resistance in OFETs, with a strong emphasis on the interplay between transistor performance (beyond mobility) and contact resistance.

Contact resistance has been a constant topic in the development of organic electronic devices, along with the synthesis of new materials, the design of better device structures, and more efficient manufacturing techniques. In Figure 1 and Table 1 we summarize the lowest reported contact resistances in OFETs over the past 20 years, from 1999 to 2019. It can be clearly observed that R_C values remained relatively constant until 2012, after which a steady decrease has occurred. This timeline correlates with the field acknowledging the impact of charge injection and collection and working toward understanding and controlling the various device factors that influence R_C . This progress in holistic device improvement is commendable, as charge carrier mobility is not a sufficient metric for emerging applications based on organic devices. The current lowest measured contact resistance for an OFET was reported by Borchert et al. as $R_C = 29 \ \Omega cm$ for bottom gate, bottom contact devices with an ultra-thin (5.3 nm) gate dielectric.^[13] This work is the culmination of a series of reports that identified the importance of the gate dielectric layer on the OFET contact resistance,^[14,15] combined with chemically modifying the contacts using a self-assembled monolayer of pentafluorobenzenethiol (PFBT). It should be noted that the devices were operated at gatesource and drain-source voltages (V_{GS} and V_{DS} , respectively) less than 3 V, produced mobilities of 5 cm² V⁻¹ s⁻¹, record subthreshold swings of 62 mV/decade, on/off ratios of 10⁹, and ring oscillator stage delays of down to 138 ns, all enhanced by low R_C . These impressive results, utilizing a variety of material and device enhancements, validate the continued research efforts to understand the complexities surrounding contact resistance in organic transistors. This value of contact resistance, however, is still an order of magnitude larger than the best in electrolyte-gated organic transistors, where $R_C = 1 \Omega$ cm was obtained as a result of strong doping of the semiconductor from the electrolyte layer,^[16] and far larger compared to contact resistances typical in silicon transistors. To guide modern electronics production, the

2013 International Technology Roadmap targeted 0.01 Ω cm to 0.015 Ω cm contact resistance for 10 nm nodes,^[17] and recent literature reports contact resistance as low as 5 ×10⁻⁴ Ω cm in Si transistors with heavily doped Ni(Pt) silicide contacts.^[18]

1.2 Signature and Consequences of Contact Resistance on OFETs

The operation of a field-effect transistor (FET) transistor has two regimes of current behavior ("linear" and "saturation") depending on the relative size of the applied voltage at the drain, V_{DS} , and at the gate, V_{GS} , when the device is operated above the threshold voltage V_{th} (i.e., $|V_{GS}| > |V_{th}|$). The equations for the drain current I_D derived from the gradual channel approximation (GCA) are used to model and analyze field effect transistors:

$$I_{D} = \mu c_{i} \frac{W}{L} \left[(V_{GS} - V_{th}) V_{DS} - \frac{V_{DS}^{2}}{2} \right], |V_{DS}| < |V_{GS} - V_{th}|$$

$$I_{D} = \mu c_{i} \frac{W}{2L} (V_{GS} - V_{th})^{2}, |V_{DS}| > |V_{GS} - V_{th}|$$
(2)

where μ is the semiconductor mobility, c_i is the dielectric capacitance per area, W the width of the channel, and L the length from drain to source. A key assumption of the GCA model is that the contacts can supply infinite current, meaning that contact resistances are not accounted for in the GCA model. (See Lamport et al. for a full discussion on the device physics in OFET behavior.^[2])

In **Figure 2** we show several examples that demonstrate the impact of contact resistance on OFET device performance and the signature in current-voltage curves. The black line in Figure 2a illustrates the dependence of I_D vs. V_{GS} (transfer curve) in the linear regime (Equation 1) for the case of ideal contacts ($R_C = 0$), where the linear I_D vs V_{GS} curve agrees well with the GCA model. On the contrary, when $R_C \neq 0$, a lower current and nonlinear transfer characteristics are obtained, depending on how R_C changes with the gate bias. Similarly, the effect of R_C can appear in the saturation regime (Equation 2); Figure 2b depicts how a large, bias dependent R_C leads to deviations from linearity in the $I_D^{1/2}$ vs V_{GS} curve.^[52,58] In this case, at low V_{GS} the channel (R_{Ch}) and contact resistances are similar and the OFET is

dominated by contacts. As the voltage increases, R_C drops and access to the channel properties is possible. Figures 2c and 2d show output characteristics where high R_C results in an S-shape of the I_D vs V_{DS} curve for low bias and a reduction in I_D (Figure 2c), or collapse of the I_D curves on top of each other at low bias and the absence of a saturation regime (Figure 2d). While in these examples the current exhibits obvious deviations from standard FET behavior, large contact resistance can also manifest as an overall decrease in current, without changing curve shape, making the impact hard to discern from simply analyzing the I-V curves.^[61]

Extrapolating standard parameters from R_C -dominated transistors leads to mischaracterization of the semiconductor, including the mobility^[52,57,58,62] and the threshold voltage,^[57,63] which are important factors in characterizing the speed and driving voltages for final circuit design. Several recent articles cover errors in the estimation of device mobility that can occur in the presence of severe contact effects, resulting in both under- and overestimation.^[52,58,62,64,65] The impact of R_C becomes more severe with the reduction of channel dimensions and increase in semiconductor conductivity. Misparameterization due to high R_C has far reaching impacts, from complex devices that don't perform as expected to materials discarded from future study due to poor device performance. This topic was thoroughly discussed in several recent articles, and we will not emphasize it here.^[52,58,62,64,65]

This review is organized as follows: we first discuss the dominant charge injection mechanisms in organic semiconductors and include an in depth discussion of the manifestation of injection limited current on OFET operation. In Section 3 we provide an overview of contact resistance measurements, and in Section 4 we review recent progress in contact design and fabrication. We end by discussing the current and future perspectives of contact improvement in OFETs and providing recommendations for areas of work that we identified as important to move progress forward.

2. Charge Injection through a Metal-Semiconductor Interface

Metal-semiconductor interfaces have been extensively studied and optimized for traditional, inorganic devices – a review of current understanding can be found in reference^[66]. While some of the physics is the same, the properties of the organic semiconductor/metal interfaces are quite different and creating a low-resistance contact is not trivial. In this section, we discuss the phenomena occurring at the interfaces between organic semiconductors and electrode materials, describe the 1-dimensional (1D) charge injection models proposed for these systems, and analyze the origin and properties of contact resistance in the context of OFETs.

2.1. The Schottky Barrier

A metal and a semiconductor (SC) typically have an energetic mismatch due to the difference in Fermi levels (E_F) of the two materials. Without surface interaction, the energetic height, called the Schottky barrier (ϕ_B), is the difference in energy between the metal work function (WF) and the semiconductor valence or conduction band for hole (ϕ_{B_P}) and electron (ϕ_{B_n}) injection, respectively. In organic semiconductors (OSCs), the barrier is formed between the metal and either the HOMO (highest order molecular orbital) or LUMO (lowest unoccupied molecular orbital) of the semiconductor for the injection of holes or electrons, respectively, see **Figure 3**.

$$\phi_{Bn} = WF - EA \tag{3}$$

$$\phi_{Bp} = IP - WF \tag{4}$$

In Equations 3 and 4, *EA* is the electron affinity and *IP* is the ionization potential. In the ideal Schottky-Mott limit, the barrier height is only controlled by the metal and semiconductor energetic levels, and will change when these levels are modified. When the metal and OSC

are brought into contact, thermal equilibrium is reached by charge carrier transfer, which leads to alignment of the Fermi energy (E_F) in the two materials, Figure 3b. While Equations 3 and 4 can be used to roughly match energy levels between metals and semiconductors, this simplified model is often inaccurate due to the complex phenomena occurring at the interface. In this section, we will discuss changes to ϕ_B that result from the inherent properties of the interface, and in Section 4 we will outline methods used to experimentally modify the Schottky barrier in OFETs.

2.1.1 Measuring the Schottky barrier

Measured Schottky barrier values range from 0.1 eV to 1 eV at interfaces between metals and organic semiconductors.^[67–69] One common method to determine the Schottky barrier is to directly measure *EA*, *IP*, and *WF* using photoelectron spectroscopy (PES). PES is a method for determining the energy levels within a material by using the photoelectric effect. High energy monochromatic light is used to excite electrons which are then emitted into vacuum, and the energies of emitted photons are then used to extrapolate the binding energies in a material. The *EA* and *IP* were shown to change as a function of OSC layer thickness, especially in the first few monolayers, hence thickness dependent measurements of OSC on metals are often used to determine the character of the interface. For a review of PES for organic molecules see reference^[70]. Ultraviolet Photoelectron Spectroscopy (UPS) provides access to *WF* under high-vacuum; however, surface contamination can shift this value significantly in devices.^[71] An alternative method for determination of *WF* uses Kelvin probes, which are typically calibrated with freshly cleaved highly oriented pyrolitic graphite (HOPG).^[72,73]

The barrier can also be derived from device measurements. Xu et al. determined the barrier between modified gold electrodes and polymer semiconductors by fitting the output characteristics to a Schottky-junction diode equation in the bias range where contacts

dominate.^[69] Sarker and Khondaker estimated the value from temperature dependent measurements of current in a pentacene transistor with carbon nanotube contacts by fitting to thermionic field emission and tunneling injection current models.^[68]

2.1.2. Formation of the Interface

At a metal-semiconductor interface the materials exchange charges to establish a common Fermi level, Figure 3b.^[74] In band-type semiconductor physics, this results in a depletion of charges near the contact from an area with width (d):

$$d = \sqrt{\frac{2\varepsilon_s}{\rho} \left(\Psi_{Bi} - V - \frac{kT}{q}\right)}$$
(5)

where ϵ_{S} is the dielectric constant of the semiconductor, ρ is the charge density in the semiconductor, V is the applied voltage at the interface, T is the temperature, k is the Boltzmann constant, q is the elementary charge, and Ψ_{Bl} is the built-in potential across the depletion region at thermal equilibrium.^[75] Across this distance, the semiconductor bands bend in response to the charge accumulation at the interface, Figure 3b. The depletion region typically extends quite far into organic semiconductors due to the small charge density. States in band gap at the interface will fill when contact between the metal and semiconductor is established and will satisfy the formation of equilibrium without shifting the Schottky barrier. This is experimentally observed as a constant Schottky barrier despite changing metal or semiconductor work function, a phenomenon known as Fermi level pinning. In this case, equations 3 and 4 will no longer apply. The states that contribute can be either intrinsic to the semiconductor or induced by the presence of a metal (see references^[11,66] for discussion of metal induced gap states/induced density of interface states).

In organic semiconductors the HOMO and LUMO transport levels are not sharply defined, but a distribution of localized tail states form in the band gap due to dynamic and static disorder, introducing ambiguity in determining the band edges.^[76,77] The shape of the

band edge distribution is often modeled as either an exponential^[78] or Gaussian^[79] tail with width σ_{DOS} . Typical values for σ_{DOS} can be on the order of 0.25 eV,^[79] a not-inconsequential fraction of the ideal Schottky barrier for a typical metal-organic semiconductor interface. Using PES measurements of the HOMO and LUMO levels, Jung et al. observed that the σ_{DOS} creates an effective HOMO (LUMO) level that is located within the band-gap, at higher (lower) levels than the peak of the HOMO (LUMO) distribution.^[80] According to Equation 3 and 4, ϕ_B is then decreased when compared to calculations using values of *EA* obtained from the HOMO peak according to the offset values for *EA* and *IE* due to the spread of energy levels into the gap. Oehzelt et al. found that a wide σ_{DOS} introduces Fermi pinning, and reducing the energetic disorder is desirable to facilitate work function matching between metal and semiconductor.^[79] Results presented by Bittle et al. for disordered polymer OFETs similarly showed that a decrease in structural disorder (that contributes to energetic disorder) corresponds with a decrease in contact resistance.^[81]

hen charges move to the surface of a metal, a space charge will build at the electrode/OSC interface, which creates an attractive force which can be modelled as the formation of an oppositely polarized "image charge". The Schottky barrier is therefore lowered by:^[75]

$$\Delta \phi_B = \sqrt{\frac{q\mathcal{E}_M}{4\pi\varepsilon_s}} \tag{6}$$

where \mathcal{E}_M is the maximum electric field at the interface. The Schottky barrier then changes as a function of applied field and doping, such that Equations 3 and 4 are modified: $\phi_{Bn} = WF - EA - \Delta \phi_B$ and $\phi_{Bp} = IP - WF + \Delta \phi_B$. While doping is an efficient way to decrease the Schottky barrier, there are considerable challenges to doping an organic device; details can be found in Section 4.3.

2.1.3. Metal-Molecule Interactions

When a molecule comes into proximity of a metal, the electron cloud that tails out of the metal surface will rearrange in response to the electron cloud of the molecule.^[82] In addition. the conformation and orientation of the organic semiconductor molecules on the metal and amount of chemical bonding can vary based on the surface energetics and chemistry, a process that also results in shifts in ϕ_{B} . ^[83] When molecules are physisorbed, they couple weakly to the metal surface and the alignment of energy levels can approach the Schottky-Mott limit where ϕ_B is controlled by the metal work function and the semiconductor HOMO/LUMO levels.^[67,84] For strong molecule-metal interactions, such as the case of chemisorbed molecules.^[85] charge transfer from the metal to the semiconductor molecules leads to the formation of large surface dipoles, making the band diagram of the isolated material surfaces irrelevant.^[84,86] The strength of the coupling between the organic semiconductor and the electrode can be tuned, to a certain extent, by processing. For example, Zimmerling and Batlogg showed that exposure of the metal interface to air before making the metal-semiconductor contact results in reduced contact resistance in single crystal rubrene OFETs with gold contacts, likely due to a contamination layer that reduces the interface interaction and charge transfer leading to a more physisorbed-type contact.^[87] The energetics at the interface and the processing steps taken to form the interface can modify the ordering of molecules into the bulk,^[67,84] introducing an additional barrier related to charge movement within the first few layers of organic material. Surface modifications can also be used to intentionally shift the work-function, tune the degree of charge transfer, and modify semiconductor conformation by applying structures like self-assembled monolayers (SAMs), dopant layers, and oxide interlayers, as we will discuss in Section 4. Predicting the interfacial energy level alignment at the organic-metal interface is not yet possible, though significant progress has been made.^[88,89] The energy band diagram should therefore be employed only as rough guide for selecting contact materials but does not guarantee efficient charge injection.

2.2. Injection Physics and Models

Injecting charges through a metal-semiconductor interface requires the navigation of the energetic barrier ϕ_B . Charges can, in simple terms, be transferred over the barrier or through the barrier; common 1D models proposed for charge injection are illustrated in **Figure 4**. The injected charge current density (*J*) typically results from a superposition of physical effects that include field emission from a metal and tunneling across the energetic barrier. Dominant injection pathways can be tuned by doping, temperature, and semiconductor mobility. In applying traditional injection models to novel organic semiconductors, inherent differences in the materials will lead to varying physics and therefore different mitigation strategies should be pursued in device development.

Charge injection at a metal/semiconductor interface depends on the electric field applied across this interface, a quantity that is difficult to measure as the injection area at the contact is extremely small. As such, the injected current behavior as a function of applied voltage is used as an approximation in order to fit experimental data. In OFETs, changes in *J* due to the presence of a gate field have also been observed that go beyond simple injection models that focus on one-dimensional fields and constant carrier concentrations. It is therefore important to note that the voltage applied in OFET measurement is a crude approximation of the electric field at the contact, and thus care must be taken in applying the existing injection models. Below is a brief introduction to dominant charge injection regimes in one-dimension with recent examples in organic semiconductors, followed by recent results specific to OFET structures.

2.2.1. Thermionic Field Emission

Thermionic field emission (TFE) occurs when the Schottky barrier height is above the thermal energy (Figure 4a). Charges in the metal with energy above the barrier height, either thermal

or from an applied field at the interface, can overcome the barrier into the semiconductor resulting in injection current:

$$J = A^* T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \exp\left(\frac{qV}{kT}\right)$$
(7)

$$A^* = \frac{4\pi q m^* k^2}{h^3}$$
(8)

where *h* is Planck's constant and *m** is the effective mass of the charge carrier in the metal.^[75] This model has been applied successfully for organic semiconductors with various contact materials, including metals, carbon nanotubes and metal-oxides.^[68,69,90] Li et al. demonstrated that the field dependence of the contact resistance follows the behavior predicted by TFE for devices with semiconductor 2,9-didecyl-dipaphtho[2,3-b:2',3'-f]thieno[3,2-b] thiophene (C₁₀-DNTT) on modified gold contacts.^[91] They also found that a small change in the work function of the contact material creates a significant change in contact resistance, hinting at the influence of the exponential dependence of *J* on ϕ_B . Sarker and Khondaker observed temperature dependent current behavior, suggesting TFE injection for pentacene with carbon nanotube contacts for T > 200 K and applied field E < 10⁶ V/cm, see **Figure 5** region I.^[68] Xu et al. found temperature dependence that matches the TFE model at T > 150 K in OFET structures of two co-polymers diketopyrrolopyrrole-thieno[3,2-b]thiophene (DPPT-TT) and indacenodithiophene-co-benzothiadiazole (IDT-BT).^[69] While these results were examined in the context of TFE, the reader is cautioned that the applied field and temperature dependence of diffusive injection follows similar behavior, as discussed below.

2.2.2. Tunneling

Provided that the organic semiconductor has sufficient empty states near the contact and the depletion region is smaller than the mean free path of charges in the semiconductor layer, charges can tunnel through the Schottky barrier. For systems with dominant TFE at room temperature, tunneling may be observed at low temperatures where TFE is suppressed, and at

high fields where the probability of tunneling is higher. Crossover from thermionic emission to tunneling has been observed for applied fields of around 10^6 V/cm in organic light emitting diodes and OTFTs.^[68,92]

Two types of tunneling exist, direct tunneling and Fowler–Nordheim (FN) tunneling. Direct tunneling is dominant at low fields, where the injection barrier is effectively "square" at the energy level that carriers are injected (Figure 4b). This results in injected current^[93]

$$J \propto V \exp\left(-\frac{2 \, d\sqrt{2m^* \phi_B}}{\hbar}\right) \tag{9}$$

where $\hbar = h/2\pi$. At higher fields, the injection barrier bends down on one side (Figure 4c) and the injected charges then experience a barrier which is "trapezoidal" in shape, resulting in Fowler-Nordheim injection current^[93]

$$J \propto V^2 \exp\left(-\frac{4d\sqrt{2m^*\phi_B{}^3}}{3\hbar qV}\right).$$
(10)

Both direct and Fowler-Nordheim tunneling was detected at the contact between pentacene and carbon nanotubes for an electrode distance of 200 nm, shown in Figure 5 regions II and III.^[68]

For very small depletion regions created through high doping ($\rho/q \approx N > 10^{17} \text{ cm}^{-3}$ in silicon),^[75] direct tunneling can be a dominant mechanism at low fields and high temperature. This is due to the reduction of the depletion region width (*d*) and change in the barrier height due to image force lowering with carrier concentration ($\Delta \phi_B \propto n^{1/2}$).^[75] See Section 4.3 for a discussion of recent work on modifications to the injection contact through doping in organic semiconductors.

2.2.3. Diffusion

Charges injected into the depletion layer at the contact can be backscattered and recombine at the metal interface when the mean free path is smaller than the depletion width, and may lead to recombination back into the injection contact (Figure 4d, dashed arrow). The charge which enters the depletion region can also be considered to have an escape probability, such that charges that escape backscatter become the current injected into the device.^[94] While this process is not conceptually parallel to injection as seen in the two models above, it is a significant modification to the charge that is injected at the contact into the bulk of the semiconductor resulting in device current. The diffusion injection current can be modelled as:^[75]

$$J \approx q\mu N \mathcal{E}_{M} \exp\left(-\frac{q\phi_{B}}{kT}\right) \left[\exp\left(\frac{qV}{kT}\right) - 1\right]$$
(11)

where *N* is the effective density of states in the conducting band, \mathcal{E}_{M} is the maximum electric field at the interface, and μ is the charge carrier mobility of the semiconductor. The *V*, *T*, and ϕ_{B} dependence is very similar to TFE, but there is an additional dependence on the mobility and carrier concentration in the semiconductor. Due to the dependence of μ on applied field in some materials, diffusion current may show enhanced bias effects.^[81,95]. Liu et al. suggested that diffusion is a dominant process in OFETs and developed a model for contact resistance in a regime where TFE and diffusion are both present.^[95] Diffusion of the carriers back into the contact has also been explored in OLEDs.^[94] While TFE is usually invoked to explain voltage and temperature dependence of injection current, observed changes to R_{C} with mobility may mean that diffusion is present in low mobility semiconductors.^[81]

2.3. Contact Resistance in OFETs

To this point, we discussed charge injection in one-dimension and we ignored the geometric and electrostatic considerations specific to FETs. While the above models are sufficient to

explain and account for certain phenomena occurring in OFETs, they do not explain more complicated behavior that arises in transistor structures. In this section, we discuss recent progress in understanding transistor-specific contact effects.

2.3.1. Origin of Contact Resistance in OFETs

The contact resistance R_C in an OFET device results from the voltage required to transfer the charges across the source contact/OSC interface and the drain contact/OSC interface. The total voltage applied between the source and drain electrodes is thus distributed across the contacts and channel:

$$V_{app} = \Delta V_S + \Delta V_{ch} + \Delta V_D = I_D (R_S + R_{ch} + R_D)$$
(12)

where ΔV_S and ΔV_D represent the voltage drops at the source and drain contacts, respectively, and ΔV_{ch} the voltage drop across the channel, **Figure 6**. R_S and R_D are the contact resistances at each terminal and R_{ch} is the channel resistance. In an ideal OFET, a very small voltage is necessary for charge injection and collection, meaning $\Delta V_S \approx 0$ and $\Delta V_D \approx 0$, therefore $R_S \approx 0$ and $R_D \approx 0$ (Figure 6a). In this case, $V_{app} = V_{ch} = V_{DS}$ in Equation 1 and 2. In real devices, however, $R_C \neq 0$; while the gradual channel approximation can still be adopted for the case when $R_C << R_{ch}$, if R_S and R_D are comparable to or larger than R_{ch} then ΔV_S and ΔV_D will be a significant fraction of V_{app} , and ΔV_{ch} will be substantially lower (Figure 6b). In Figure 6c we include the simplified equivalent circuit of an OFET, with $R_C = R_S + R_D$, and $R_{ch} = R_{ch}(L)$. With a reduction in R_{ch} by increasing the intrinsic mobility of the organic semiconductor and/or scaling down the channel length, ΔV_{ch} decreases without a comparable change to the contacts. In the extreme case, ΔV_D and ΔV_S will overwhelm ΔV_{ch} and the device will be dominated by contact resistance.^[10] In this case, Equation 1 and 2 become irrelevant and their adoption leads to mischaracterization of the device properties.

Sweeping the gate bias modifies the resistance of the channel by shifting the Fermi level in the semiconductor. Gate bias can also drive the injection current, resulting in a gate

bias dependent contact resistance. Uemura et al. and Bittle et al. analyzed the current-voltage characteristics in OFETs with an exponentially V_{GS} dependent injection current and found that such devices are dominated by contact effects at low gate bias.^[52,58] The problem can be exacerbated by semiconductors with voltage dependent mobility, where the contact resistance induced non-ideality of the I-V characteristics becomes more severe.^[57] For devices with a low mobility region near the contact, Li and Bredas suggested that the device can be dominated by the contact at higher gate bias.^[91]

The contact resistance of an OFET is dependent on the nature of the electrode and semiconductor materials, physics of the injection interface, and device related parameters:

$$R_C \propto R_C(\varphi_B, E, T, L_0, \mu) \tag{13}$$

where L_0 is the distance from the electrode to the accumulation channel, and the charge carrier mobility μ of the organic semiconductor is defined both in the direction perpendicular to the channel μ_{perp} and across the channel $\mu_{parallel} = \mu_{FET}$. Many of the parameters are interdependent and will have varying levels of influence depending on the specifics of the interface and device being studied. This complex picture can make disentangling dominant injection regimes difficult.

2.3.2. Geometric Considerations in an OFET

In Section 2.2 we discussed charge injection in the 1D case and with only one voltage applied. Field-effect transistors allow for independent control of a second voltage, the gate voltage. The gate field introduces a second component of the electric field that contributes to the net effective applied field at the contact \vec{E}_{net} . In the following, we will refer to the electric field created by the source-drain voltage (V_{DS}) as \vec{E}_{\parallel} , since it is parallel to the device channel, and the electric field perpendicular to the channel and created by the source-gate voltage (V_{GS})

will be labelled \vec{E}_{\perp} . The net electric field experienced by the injected charges is the vector sum

$$\vec{E}_{net} = \vec{E}_{\parallel} + \vec{E}_{\perp}.$$
(14)

Note that \vec{E}_{\perp} is several orders of magnitude higher than \vec{E}_{\parallel} near the contact due to the fact that the distance between the gate and the source, given by the dielectric thickness, is typically much smaller ($t \approx 2.5 \text{ nm}^{[96]}$ to 1 µm) than the drain-source distance ($L \approx 100 \text{ s of nm}^{[68,97]}$ to 10s of µm).

The basic geometries of common FET structures are shown in **Figure 7** and **Figure 8**. Electrostatically, the transistors can be considered as either coplanar or staggered. Coplanar FET geometries have the source, drain, and gate contacts on the same side of the semiconductor and are termed BGBC (bottom gate, bottom contact – Figure 7a) or TGTC (top gate, top contact – Figure 7b). For staggered geometries, the source and drain contact are located on one side, while the gate electrode is on opposite side of the semiconductor, referred to as TGBC (top gate, bottom contact – Figure 8a) or BGTC (bottom gate, top contact – Figure 8b).^[2] Processing order of the device layers can affect the semiconductor/contact interface and introduce additional disorder near the contact or implantation of metals into the semiconductor. Due to the different injection site geometry and processing conditions for coplanar vs staggered devices, the origins of contact resistance and mitigation strategies also differ.

In coplanar devices (Figure 7), charges are predominantly injected at the edge of the source contact; therefore, the metal/semiconductor injection interface is approximately given by the lateral area of the electrode (channel thickness times the channel width). The injected current, *J*_{int} flows in the same direction as the overall device current, *J*_{FET}. On the other hand,

in staggered devices (Figure 8) the charges are typically injected over a larger area (roughly given by the product between the channel width and the source to gate overlap, L_{ov}). The injected current moves towards the dielectric, perpendicular to the device current, through the thickness of the semiconductor beneath the contacts L_0 . Depending on the relative values of R_C and R_{ch} , the effective injection area can become smaller, with the regions of the electrodes closer to the channel injecting more charges, a phenomena referred to as current crowding.^[98] In addition, as L_{ov} is decreased, the contact resistance increases.^[39,99] Ante et al. found that R_C increased by an order of magnitude when L_{ov} is smaller than the carrier transfer length (the length near the contact through which 63% of charge is transferred), as compared to when L_{ov} is much larger than the carrier transfer length.^[39] If there is substantial charge transport anisotropy in the semiconductor ($\mu_{perp} << \mu_{FET}$), or for the case of thick semiconductor layers, the transport through the bulk to reach the gate interface is very inefficient and can lead to a large R_C and transport characteristics that do not fit the standard TFT model.^[91]

To achieve high operational speeds, the length of the overlap between the gate and drain/source contacts L_{ov} , shown in Figure 7c and Figure 8c, needs to be minimized to reduce the capacitance of the contact. While this would increase device speed, in staggered geometries Natali et al. found that there is a minimum contact length to allow for enough area such that there is sufficient current to operate the device.^[99] Assuming that the mobility is isotropic, in order to achieve $R_C \leq 10$ % of R_{tot} they suggested that L_{ov} should be 1.5 times larger than the injection length (or transfer length), and that L should be 18 times larger.^[99]

2.3.3. Interface and Bulk Contributions to the Contact Resistance

The contact resistance can be expressed as the sum between the resistance associated with the injection barrier $R_{C,int}$ and the bulk resistance $R_{C,bulk}$ associated with charge transport through length L_0 (see Figure 7d and 8d)

$$R_C W = R_{C,int} W + R_{C,bulk} W \tag{15}$$

where the contact resistance is normalized to the transistor width, W.^[44,90,100] The second term is zero for the case of coplanar contacts since they inject directly into the channel.

In a model originally used for amorphous silicon^[100] and modified for organic devices,^[44] Equation 15 becomes:

$$R_{C}W = R_{C,int}W + \frac{L_{0}}{\mu_{perp}c_{i}(V_{GS} - V_{th})}.$$
(16)

Here the injection resistance is treated as a constant, while the bulk component is dependent on the semiconductor mobility in the direction perpendicular to the device channel and the effective gate voltage. When mobility through the thickness of the semiconductor, μ_{perp} , is independent of the gate voltage, the contact resistance is proportional to V_{GS}^{-1} . For $\mu_{perp} \propto V_{GS}^{\beta}$, as for the case of energetically disordered materials,^[76,77] contact resistance then varies as $V_{GS}^{-(\beta+1)}$. This model can, in principle, also be extended to modeling coplanar structures with a low mobility region near the injection interface (e.g. due to localized disorder) by replacing μ_{perp} and L_0 with mobility and length of the region. To model the injection resistance explicitly, Li et al. proposed and found experimental agreement for an explicit treatment of the injected current (R_CW)_{int} with constant bulk resistance by applying an electric field enhanced thermionic emission model to the injection barrier, such as

$$R_C W = A \frac{\left(B\sqrt{V_G - V_{th}}\right)^2}{\exp\left(B\sqrt{V_G - V_{th}}\right)} + R_B W$$
⁽¹⁷⁾

where the fitting coefficients A and B depend on the energy barrier ϕ_B and the strength of the electric field dependence respectively.^[90] Both Equation 16 and 17 illustrate the gate bias dependence of the contact resistance, but they place the mechanism within the bulk or directly at the injection site. As seen in **Figure 9**, the two extremes are demonstrated by modifying the

injection interface and thickness of the semiconductor in a staggered geometry, thereby showing the relative influence of $R_{C,int}$ and $R_{C,bulk}$ on R_{C} .^[90] The choice of model is dictated by whether the bulk or injection interface is more influential for a given transistor, and by the dominant injection mechanism.

2.3.4. Influence of the Gate Dielectric Layer on Contact Resistance

The literature reports on the impact of the gate dielectric properties on the operating voltages of the OFETs,^[101] microstructure of the semiconductor film,^[102] interfacial trap density,^[103,104] bias stress stability.^[105] and more. It was recently discovered that the dielectric layer can also impact the contact resistance. In 2013, Gruber et al. performed drift-diffusion calculations that suggested that coplanar bottom contact devices could outperform staggered top contact devices given sufficiently small injection barrier and high gate-source voltages.^[14] This was confirmed by further simulation in 2015 by Zojer et al. who showed the differing injection behavior between BGTC and BGBC devices: the contact voltage is nearly constant in the BGTC structure, which leads to a decrease in device mobility, while the contact voltage in BGBC devices is strongly gate-field dependent.^[15] In other words, the BGBC structure takes greater advantage of a strong field at the semiconductor/dielectric interface. To increase the strength of the field generated by V_{GS} , high-k dielectrics and/or a thin dielectric layer can be used. A solution is to use a thin layer of aluminum oxide passivated by an alkylphonsphonic acid SAM for a dielectric thickness down to 5.3 nm.[13,96,106,107] BGBC OFETs of 2,9diphenyl-dinaphtho[2,3-b:2',3'-f] thieno[3,2-b]thiophene (DPh-DNTT) with SAM gate dielectric, and PFBT-treated gold source and drain contacts produced lower R_C (29 Ω cm) compared to the BGTC counterpart (56 Ω cm), and was the first experimental validation of the aforementioned theoretical predictions.^[13]

Increasing contact resistance due to the presence of traps at the dielectric/electrode interface has been observed by Liu et al.^[44] and Paterson et al.^[108] This effect was assigned to

the reduced number of mobile carriers near the contact, resulting in formation of space charge region and field screening in the staggered geometry.^[44] Kim and Horowitz developed a fully analytical model for R_C evaluation that not only included the contributions from the dielectric layer, but also the semiconductor mobility, injection barrier, and the effective density of states at the frontier orbital.^[109]

3. Characterizing Contact Resistance in OFETs

In this section, we provide an overview of common methods to determine contact resistance in OFETs, including the gated transfer length method (Section 3.1), four-point probe measurements (Section 3.2), impedance spectroscopy (Section 3.3), and scanning Kelvin probe microscopy (Section 3.4). Since contact resistance can have an enormous impact on OFET function, it is important to be able to accurately measure R_C for evaluating the effectiveness of strategies to increase the performance of the contacts (Section 4) and for informing future OFET design. The gated transfer length method is the most popular method to evaluate R_c , and we discuss the theory behind this method as well as deviations from and improvements to the model. Four-point probe methods use a separate set of voltage sensing contacts that are disentangled from charge injection and provide independent measurement of contact resistance for the source and drain. Impedance spectroscopy relies on fitting timeperturbed measurements to equivalent circuit models, but this comes with its own challenges as we will discuss in Section 3.3. Finally, scanning Kelvin probe microscopy is explored in detail for characterizing OFET behavior at the contact/semiconductor interface, including a few recent developments in the technique. For additional information and a tutorial on select methods, the reader is referred to the review by Lamport et al.^[2]

3.1. Gated Transfer Length Method (gTLM)

The gated transfer length method (gTLM), also referred to as the gated transmission line model,^[110] is a method to extract R_C from current-voltage characteristics of a set of devices

with varying channel length. The model assumes that the device is Ohmic, the mobility is constant across all investigated devices, and the applied voltage is of the form depicted in Figure 6b, meaning that it is dropped across three resistances in series: the source, channel, and drain (Figure 6c). Contact resistance R_C encompasses the contributions from both the source and the drain so the total device resistance is $R_{tot} = R_{ch} + R_C$. (Note that there's some inconsistency in the literature on the use of the term R_C to mean the contact resistance of only one contact or the total contact resistance; here we use it to refer to the sum of the source and drain contact resistances $R_C = R_S + R_D$.) By changing the length of the channel, R_{ch} is varied while R_C is held constant for a given effective gate voltage. The model also assumes that the organic semiconductor film is uniform, R_{ch} scales linearly with channel length, and R_C remains constant for all lengths. Linear $R_{ch}(L)$ dependence can be easily understood by applying Ohm's Law to Equation 1:

$$R_{ch} = \frac{L}{\mu W c_i (V_{GS} - V_{th})}.$$
(18)

Adding the channel resistance to the contact resistance and multiplying by W gives the widthnormalized total resistance of the device:

$$R_{tot}W = \frac{L}{\mu c_i (V_{GS} - V_{th})} + R_C W.$$
 (19)

As the channel length *L* is decreased, the total resistance will approach $R_{tot} = R_C$. The quantity $R_{tot}W$ is calculated for a series of devices with different channel lengths, biased at the same effective voltage $V_{GS} - V_{th}$, and the results are extrapolated to L = 0 to obtain the width-normalized contact resistance R_CW (see Figure 10).

There are a few methods used for determining R_{tot} .^[2,24,39,111,112] One common method relies on extracting the slope of the I_D - V_{DS} curves in the linear regime for a given effective voltage $V_{GS} - V_{th}$,^[24] while another requires taking a specific point on the I_D - V_{GS} curve at a known V_{DS} and applying Ohm's Law.^[2] As the channel resistance is a function of the effective gate voltage $V_{GS} - V_{th}$, and the threshold voltage can vary significantly among devices that are

nominally the same, the second method listed here makes it easier to compensate for shifting threshold voltages by analyzing the different devices at a fixed value of $V_{GS} - V_{th}$ known as the overdrive voltage.^[2,39] Adjusting for a shifting V_{th} in extrapolating R_{tot} is made more difficult by the fact that V_{th} inherently shifts with V_{DS} , more so at shorter channel lengths.^[75,113]

Gated TLM is a very popular method adopted for the evaluation of contact resistance in organic transistors, but lateral variations in film properties and non-idealities in currentvoltage characteristics may lead to errors. Additionally, the assumption that R_{tot} scales linearly with channel length is not always valid in OFETs.^[114] In the case of staggered contacts, for example, the bulk contribution of the contact resistance, $R_{C,bulk}$, can exhibit a non-linear behavior with the applied voltage due to space charge limited current effects.^[115–118] An example is provided in Figure 10, where evaluation of R_C based on the R_{tot} at long channel lengths (red slope) yields artificially lower R_C than extrapolation at short channel lengths (blue slope). In these cases, we recommend a conservative estimation of R_C , based on low Lregion. Inhomogeneity in the thin film will also skew results, an effect which is not as pronounced in single crystal devices.^[56,119]

One of the signatures of severe contact effects is the presence of non-linear I_D - V_{DS} curves at low V_{DS} , as introduced in Figure 2c and 2d. A large Schottky barrier, hence large R_C , often causes a non-linear turn-on as the injected current follows Equation 7 and 11, with $J \propto e^V$ dominating I_D . Such devices exhibit "S-shaped" output curves. This feature poses serious challenges for the extraction of R_C regardless of the method that is adopted. For the first method of R_{tot} extraction discussed, there is no longer a clear linear portion of the I_D - V_{DS} curve to fit a slope. For the second method, a large R_C introduces non-ideality into the I_D - V_{DS} curves and ambiguity in V_{th} values extracted from transfer curves. At large V_{DS} values, used to decrease the non-linearity of the curves, drain resistance will also be modified through pinch-

off effects which create a varying depletion region near the contact. These effects make it difficult to compare R_C values when different values of V_{DS} are used for gTLM.

Various solutions for improving the accuracy in the evaluation of R_C from I-V curves have been proposed.^[113,120–128] Xu et al. created a modified gated transfer length model (M-TLM) that takes advantage of the fact that the slope of the linear fit is less sensitive to variations in data than the intercept.^[120] In this method, Equation 19 is divided by *L* and the quantity $R_{tot}W/L$ is plotted against 1/*L*. This way, R_CW is now the slope of the plot and $R_{ch}W$ is the intercept. In tests on randomly generated data, M-TLM more closely predicted the given contact resistance and with a better standard deviation than when compared with conventional gTLM. Another improvement for gTLM includes the dependence of V_{th} on L.^[123] Other methods rely on developing transistor equations beyond the gradual approximation model. Di Pietro et al. formulated a model starting with charge-density dependent mobility and contact resistance to extract device parameters from I_D vs V_{GS} plots.^[122] Krammer et al. demonstrated the limitations of gTLM using a combined theoretical and experimental effort, and developed a new method called the two-step fitting approach (TSFA).^[113] Based on a rigorous model of OFET operation, the parameters given by TSFA gave a much better fit to experimental data than parameters extracted through conventional gTLM, especially at short channel lengths.

3.2. Four-Probe Current-Voltage Measurements

Four-point probe methods encompass I-V measurement techniques that include additional voltage sense probes. By separating the voltage sensing contacts from the current injecting/collecting contacts (i.e. source and the drain), contact resistance effects associated with charge injection are minimized in measurement. Along with allowing a more precise determination of the semiconductor parameters (i.e. mobility), a great advantage of the four-point probe is the ability to separately measure *Rs* and *RD*. This is particularly useful when studying source and drain contacts made from different materials.

The geometry for the four-point probe measurements is similar to the traditional twoprobe transistor but with two additional contacts deposited in the channel of the transistor between the source and drain, at distances of L_1 and L_2 away from the source with $L_1 < L_2$. Assuming a linear drop in voltage between the injection and drain contacts, the potential drop across the channel can be calculated as

$$\Delta V_{ch} = \frac{V_2 - V_1}{L_2 - L_1} L \tag{20}$$

where V_1 and V_2 are the measured potentials at L_1 and L_2 , respectively. This expression, along with the geometry of the device, gives the information needed to calculate the potential drop across the source and drain. The voltage drop across the source, ΔV_S (see Figure 6b), is

$$\Delta V_S = \left(V_1 - \frac{V_2 - V_1}{L_2 - L_1} L_1 \right) - V_S.$$
⁽²¹⁾

Typically $V_S = 0$ V. Similarly, ΔV_D , the potential drop across the drain, is calculated as

$$\Delta V_D = V_D - \left(V_2 + \frac{V_2 - V_1}{L_2 - L_1}(L - L_2)\right).$$
⁽²²⁾

Finally, to calculate the resistance associated with each of these potential drops, use Ohm's Law with the drain current:

$$R_i = \frac{\Delta V_i}{I_D}, \quad i = S, D.$$
⁽²³⁾

More information can be found in the works by Chesterfield et al.^[23] and Pesavento et al.^[129]

Similar togTLM, the four-probe methods have their own limitations. For instance, it is only valid in the linear regime: when a transistor is operated in the saturation regime, the steep potential drop near the drain from pinch-off invalidates the assumption of a linear drop in voltage across the channel (for an example of the pinch-off voltage profile, see **Figure 11** in Section 3.4). The voltage sensing probes are ideally point-like in order to not affect the surrounding electric field; in reality, the sense probes can cause significant perturbations in the field and affect the accuracy of the measurement.^[130] The metallic probes form an

equipotential across the length of the contact, hence more voltage is dropped across the remaining regions of the channel with a corresponding increased field strength. Choi et al. have shown that this longitudinal channel shunting can lead to overestimation of mobility, sometimes by up to a factor of two or three.^[65] To mitigate this effect, sense probes are designed to be smaller than the width of the channel, though some perturbation will still remain.

Although it does not measure contact resistance, a variation of the four-point method known as gated van der Pauw (gVDP) provides access to the semiconductor mobility nearly independent of contact resistance.^[131] In this method, four small contacts are placed at corners of the semiconductor: two adjacent contacts act as the source and drain, and the other two contacts act as voltage sense probes. Rolin et al. demonstrated that contact resistance can vary by over four orders of magnitude with little effect on measured semiconductor mobility when using gVDP.^[131]

3.3. Impedance Spectroscopy

For dynamic measurements of device performance, impedance spectroscopy (IS) has proven to be a powerful tool for characterization.^[29,58,132–136] It is a frequency-dependent method of measuring the linear response of the transistor: devices are configured in a DC steady-state (for instance, with *V*_{GS} and *V*_{DS} held constant) while a time-varying perturbation is added to an input. The complex impedance of the device is measured as a function of the frequency of the perturbation. The results are then fitted to an equivalent circuit model, with fitting parameters yielding the values for circuit components, such as contact and channel resistance and capacitance.^[29] IS measurement is relatively simple, though obtaining signal from the OFET without significant impact from extraneous sources can be challenging and requires careful device design and background noise cancellation. In particular, systematic noise is present from the drain- and source-to-gate overlap region, and even from the electrical lines

connecting the device to measurement equipment. Developing an equivalent linear circuit capable of modeling a OFET is also complex, though several models are available in literature: circuits modeling the contacts as resistors and capacitors in parallel and the channel as a distributed network of resistors and capacitors have been the most popular and robust,^[29,58,133] while other methods such as s-parameter characterization have been applied as well.^[137,138]

3.4. Scanning Kelvin Probe Microscopy (SKPM)

Scanning Kelvin probe microscopy (SKPM), otherwise known as Kelvin probe force microscopy (KPFM), allows direct access to the potential drop across the contact/semiconductor interface. A necessary assumption is that the potential at the top of the device is equivalent to the potential in the channel, which is well-supported.^[139] Based on traditional atomic force microscopy, SKPM measures the contact potential difference (CPD) between the sample and the SKPM tip as a function of XY position. Here, CPD is the potential difference between two points in vacuum close to the surfaces, with the assumption that the two surfaces are in thermodynamic equilibrium. When the SKPM tip comes close to the surface, the potential of the surface induces a charge of opposite sign on the tip, creating an attractive force F_{el} . Most SKPM measurements drive the cantilever near its resonance frequency and use the perturbations due to F_{el} to find the CPD. The force is described as

$$F_{el} = \frac{1}{2} \frac{\partial C}{\partial z} \,\Delta V^2,\tag{24}$$

which is dependent on the potential difference between the two surfaces ΔV and the rate of change of the capacitance between the tip and the sample *C* with respect to the tip-to-surface distance *z*. This formulation is derived by assuming a system of two metallic parallel plates, but some have argued that the SKPM/sample system is more accurately described by a round metallic sphere (the SKPM tip) and a sheet of charge sandwiched between two layers of dielectric.^[140,141]

The use of SKPM in conjunction with OFETs started with the pioneering work of Bürgi et al., who studied the effect of gate-source and drain-source bias on the mobility of P3HT transistors.^[139] The method was quickly adopted to other OFETs.^[22,59,142,143] SKPM measurements are carried out on a biased device, and the probe scans from the contact into the channel. For a large R_C a large potential drop near the contact is observed as seen in Figure 11a. The difference between the voltage level at the plateau at the voltage at the start of the channel determines the voltage dropped across the contact, sometimes termed ΔCPD . To get the associated contact resistance, divide by the drain current:

$$R_C = \frac{\Delta CPD}{I_D}.$$
 (25)

The same method can be used to find the channel resistance by measuring the linear voltage drop in the region between the contact voltage drops. A great advantage that SKPM shares with four-probe techniques is the ability to separately measure R_S and R_D , though SKPM can also be used in the saturation regime since it can resolve the potential drop across the entire length of the channel and the contacts, allowing for the direct measurement of the pinch off region. An example is included in Figure 11b, where the potential profile of an OFET operating in the saturation regime is included and the pinch-off and contact resistance can be observed.^[51]

The most common measurement scheme for SKPM is a two-pass approach: the topography of the sample is measured on the first pass, and then the potential profile is measured on the second pass while keeping the SKPM tip at a fixed distance from the surface. However, it was noticed that after a biasing cycle trapped charges in the OFET channel will interact with the SKPM tip during the topography pass, pushing or pulling the tip away or towards the surface by sometimes more than 100 nm.^[51,141] Then, while mapping the potential profile, the tip-to-sample height is not fixed and causes substantial error. Bercu et al. solved

this dilemma by applying a gate bias during the topography scan to clear the traps, recovering the topography profiles of a device that has not been biased.^[141]

Another improvement in SKPM is to switch from the conventional method based on F_{el} to a method based on the gradient of the force dF_{el}/dz .^[51,144] Obtaining reliable quantitative results with conventional SKPM is difficult, owing to the complex interaction between the cantilever and the sample, but de Tournadre et al. found that the force-gradient method yielded accurate measurements on samples where conventional SKPM had an error on the order of 10 %.^[51] Furthermore, the force-gradient method allowed measurements at high V_{DS} (up to -35 V). During their investigation, they found linear contact characteristics in coplanar devices based on dinaphtho[2,3-b:20,3-f]thieno[3,2-b]thiophene (DNTT) and non-linear contact characteristics in staggered devices based on polytriarylamine (PTAA), with R_C values of 1 M Ω cm and 131 M Ω cm, respectively.^[51] The scans allowed for a deeper perspective of the magnitude of R_C in the coplanar devices since both R_C and R_{ch} could be accurately evaluated: 10 % of the source-drain bias was dropped over the source contact in the linear regime and up to 50 % in the saturation regime, highlighting significant injection issues that were not immediately apparent in the transistor IV curves.^[51] A similar effect was observed by Teague et al., who detected voltage drops as high as 5 V (50 % of the total applied voltage) at the source contact in single crystal devices with almost ideal output characteristics.^[61] This result emphasizes the fact that while non-ideal current-voltage curves can signal contact issues, data that follow Equations 1 and 2 do not guarantee efficient contacts.

The trend of R_C vs. V_{DS} has not been as extensively studied as R_C vs. V_{GS} , but through SKPM Chiarella *et al.* found that R_C decreased with increasing V_{DS} in an exponential fashion.^[145] Contact resistance had a stronger dependence on V_{DS} than V_{GS} , a trend also found by Chianese et al.^[145,146] Furthermore, both studies found that R_D was substantially greater

than R_s , indicating that their n-type devices were not injection limited as could be first expected of a device with high R_c .^[145,146]

The vast majority of SKPM measurements on OFETs use a statically biased device, but there is much to learn by incorporating time-dependent techniques, especially when investigating properties like switching characteristics. Murawski et al. devised a pump-probe SKPM (pp-KPFM) method that pushes time resolution into the nanosecond regime.^[147] The pump is a voltage pulse delivered to the drain electrode while the probe is a much shorter voltage pulse applied to the SKPM tip in addition to the normal sinusoidal driving voltage. The probe can be delayed to map charge transport through the channel.

4. Reducing Contact Resistance: Electrode Design and Beyond

4.1. Choosing the electrode material

As discussed in Section 2.1, a Schottky barrier is usually formed at the interface between a metal and a semiconductor brought into contact and the details of this barrier dictate the efficiency of charge injection. In a simple picture, for a given organic semiconductor with known HOMO and LUMO energies, the Schottky barrier can be tuned by the choice of metal: aligning the metal work function with the HOMO level promotes hole injection, while alignment with the LUMO allows for electron injection, leading to p-channel or n-channel OFETs, respectively. A wide selection of work functions exist: for example, calcium, lithium, cerium, and zinc can provide low work functions (2.87 eV, 2.93 eV, 2.9 eV, and 3.63 eV, respectively), while gold, nickel, palladium, platinum, and iridium have high work functions (5.1 eV, 5.2 eV, 5.22 eV, 5.64 eV, and 5.67 eV, respectively). (Note that work function is a surface property and can vary substantially with crystal plane, oxidation state, surface preparation, and cleanliness. In particular, the work function of gold has been measured to be between 4.8 eV and 5.4 eV.^[148–150]) Indeed, silver (4.26 eV) and aluminum (4.05 eV) electrodes were used for the fabrication of n-type OFETs based on P(NDI2OD-T2) and C₆₀, which both have LUMO levels of 4 eV,^[151–155] while Au electrodes were

incorporated in p-type OFETs made with 2,8-difluoro-5,11-bis(triethylsilylethynyl) anthradithiophene (diF-TES-ADT) (HOMO at 5.02 eV) and C8-BTBT (HOMO at 5.20 eV).^[32,73,156–158] One might notice that all the listed low-work function metals are elements that are fairly reactive, while most of the high-work function materials listed are noble metals. This is not coincidence: the lower the work function of a metal, the easier it is for electrons to react with ions and molecules in the atmosphere or the semiconductor itself. This makes the task of creating an air-stable contact for n-type devices quite challenging. Several approaches were successful, as we will later describe in detail. Following this simple injection picture, in the absence of other factors, contact selection would determine whether a p-type or n-type OFET device behavior is obtained by controlling the dominant injected charge carrier. For instance, rubrene (HOMO 5.36 eV, LUMO 3.15 eV) created p-channel OFETs with Au source and drain contacts, and n-type OFETs with Ca electrodes.^[159] Silver, with a work function placed squarely between the HOMO and LUMO levels of rubrene at 4.26 eV, yielded ambipolar transport but with hole and electron mobilities over an order of magnitude smaller than the in the corresponding unipolar devices due to the larger injection barrier.^[159,160] A similar effect was observed in OFETs fabricated on single crystals of DBTTF:TCNQ (dibenzotetrathiafulvalene - 7,7,8,8-tetracyanoquinodimethane) with source and drain consisting of charge transfer complexes: by changing the composition of the charge transfer (donor and acceptor molecules, and the stoichiometry), Takahashi et al. tuned the electrode Fermi energy and modulated the transport from pure n-type, to weak n-type, ambipolar, weak p-type and highly efficient p-type.^[161] A correlation between the electrode work function, contact resistance and device performance was also reported by Bürgi et al. in P3HT OTFTs (HOMO 5.0 eV), with the gold contacts (WF 5.2 eV) giving $R_C = 5 \text{ k}\Omega \text{cm}$, silver contacts (WF 4.9 eV) $R_C = 15 \text{ k}\Omega \text{cm}$, while aluminum contacts (WF 4.05 eV) increased injection resistance so much that the devices barely passed any current and R_c could not be characterized.^[142] A similar trend was observed by Kim et al., who tested Au, Ag, and Cu

(*WF* 4.65 eV) contacts for diF-TES-ADT transistors and found good performance with Au and Ag contacts – with Au outperforming Ag – but no transistor behavior with Cu contacts.^[149] However, all contacts yielded substantial improvements in current injection and contact resistance with the application of a self-assembled monolayer, as will be discussed in Section 4.2.

Work function matching is a good strategy to selecting a contact material, but most often unexpected results arise from the complexities of interface formation. For instance, Nichols et al. tested pentacene transistors with asymmetric contacts: in one case nickel and palladium contacts, and in the second case platinum and palladium contacts.^[59] As may be expected for the platinum/palladium device, larger drain currents and better overall device mobility occurred with platinum as the source contact, which can be attributed to its higher work function. With the nickel/palladium device, however, the device performed significantly better when palladium was the source, even though nickel and palladium have nearly matching work functions. SKPM scans showed a significant drop in potential across the nickel source contact, evidence of large contact resistance. This was attributed to possible oxidation of the nickel and/or non-ideal semiconductor morphology influenced by the nickel surface. Gundlach et al. found similar disparities in top-contact pentacene devices, testing gold, copper, nickel, and indium (*WF* 4.09 eV), Figure 12.^[25] Compared to the HOMO level of pentacene (4.9 eV), both nickel and gold should make good injection electrodes, but gold far outperformed nickel as a contact material. Interestingly, devices with copper contacts had drain currents nearly equal to those with gold contacts, although both the copper and nickel contact output characteristics showed an "S-shape" at low V_{DS} , an indication of significant R_C . Devices with indium contacts exhibited very limited transistor behavior, which may be expected from its low work function. The authors pointed out that indium tended to "ball-up" on pentacene,^[25] and so even a large energy-level mismatch may not completely explain poor injection.

Reducing the Schottky barrier is key for reducing the contact resistance. Matching the work function to the HOMO or LUMO band is an excellent place to start and may serve as a guide to contact selection, but as has been noted, it does not guarantee good injection. When metals fail to provide an efficient contact, different materials and approaches must be used. In the following sections, we outline methods to tune the contact interface and lower the Schottky barrier and contact resistance. One very effective method is to insert a layer of material between the metal and the semiconductor, i.e. an interlayer, which may include selfassembled monolayers (SAMs) (Section 4.2), dopants (Section 4.3), and oxide films (Section 4.4). These groupings partially overlap, but they can generally be separated based on the primary means of modifying the injection barrier, either through a dipole (SAMs) or a chargetransfer mechanism (doping and oxide films). Oxide films are often considered a subset of doping, but they have properties and a history that deserve special focus. Finally, it is important to recognize that any interlayer will change every aspect of the interface, including the interface dipole, degree of charge transfer, and sometimes even the microstructure of the semiconductor layer. It is an extremely complex system, but the past two decades have seen remarkable progress in optimizing the interface and reducing contact resistance through these methods.

4.2 Self-assembled Monolayers

Self-assembled monolayers (SAMs) are often used to modify the work function of metals to reduce contact resistance and aid in charge injection. Their ease of processing and rich chemistry have made them versatile tools for OFET fabrication. SAMs adhere to a surface via the formation of a covalent bond between the surfactant molecule and the substrate, which leads to the creation of a monolayer.^[162] For example, the most common SAMs used for contact modification in OFETs have a thiol end-group (-SH) which allows them to covalently bond to gold through an Au-S bond. The degree of order within the monolayer is determined

by the surface bond, intermolecular forces between other SAM molecules, and interactions with the solvent and environment. When placed on a surface, SAMs alter the work function by contributing their own intrinsic dipole to the local electric field, as well as by creating a dipole at the bonding site (e.g., the dipole of a gold-sulfur bond).^[163] The direction and strength of the dipole dictates the degree of the work function shift, and therefore influences the p- or n-type device behavior. Typically, SAMs containing electron-donating terminal groups (-H, -NH₂) exhibit dipole moments pointing towards the end-group, thus reducing the work function. On the contrary, SAMs with electron-withdrawing terminal groups (-F, -Cl, -NO₂) have the internal dipoles pointing towards the electrode surface and increase its work function. Roh et al. successfully modulated the channel type (p- or n-type) in poly{[N,N'bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicar-boximide)-2,6-diyl]-alt-5,5' -(2,2' bithiophene)} (P(NDI2OD-T2) or Polyera ActivInk N2200) OFETs by selecting either a thiophenol (TP) or a pentafluorobenzene thiol (PFBT) SAM, Figure 13a-c.^[164] Using silver printed electrodes with a nominal work function of 4.91 eV, TP treatment yielded a work function of 4.66 eV, close to the 4.0 eV LUMO of the semiconductor and resulted in n-type transport, while PFBT shifted the work function to 5.24 eV, close to the 5.6 eV HOMO level, giving p-type transport.^[164] The position of the substituent and the order within the SAM layer also play an important role.^[148] Ward et al. found work function shifts of 0.01 eV, 0.07 eV and 0.43 eV in OFETs with Au contacts treated with mono-fluorinated benzene thiols with the -F atom located in positions 2, 3 or 4 on the benzene ring, respectively.^[73] Consequently, the contact resistance decreased from approx. 1 M Ω cm to 10 k Ω cm. PFBT is a popular SAM incorporated in p-type OFETs. It is also a fluorine-substituted SAM but containing five -F atoms on the benzene structure, and it can increase the work function of gold by up to 0.8 eV.^[13,55,135,149,163–170] Other heavily fluorinated SAMs include 4-(tri- fluoromethyl)benzenethiol (TFBT) and 2,3,5,6-tetrafluoro-4-(trifluoromethyl)- benzenethiol (TTFP), which were shown to increase the work function, lower contact resistance, and improve OFET

performance, as seen in Figure 13d.^[171] While the fluorinated SAMs are popular choices for increasing the work function, several SAMs have been successfully adopted to reduce the work function. For example, the dimer bisjulolidyldisulfide (commonly known as Juls) reduced the work function of gold contacts from 4.95 eV to 3.77 eV, a significant 1.18 eV shift that improved the functioning of n-type OFETs based on N2200.^[172] The dimer is held together by a sulfur-sulfur bond that splits upon bonding with gold to create two SAM molecules, combining the benefits of greater stability and shelf-life of the dimer with the dipole of the monomer.^[172] The work function of silver was reduced from 4.80 eV to 3.79 eV with a one minute treatment with the same compound.^[172] Fine-tuning the work function shift can be achieved by employing SAM mixtures.^[173–177] Xu et al. blended two SAM molecules with dipoles oriented in opposite directions (1-decanethiol (1DT) and 1H,1H,2H,2H-perfluorodecane- thiol (PFDT)) in various ratios and gradually shifted the work function of gold from 4.5 eV to 5.7 eV, Figure 13e.^[173] Consequently, these contacts were used to access both n-type and p-type transport in F8BT OFETs with HOMO/LUMO levels of 5.9 eV and 3.3 eV.

The SAM molecular dipole is important; however, the tilt angle, the packing density, and degree of order in the SAM layer can lead to work function shifts as large as a few tens of eV for the same compound. The shift in work function is proportional to the sum of the net component of dipole that is perpendicular to the interface $\mu_{\perp,SAM}$ and the bond dipole $\mu_{Metal/SAM}$:

$$\Delta WF \propto \frac{\mu_{\perp,SAM}}{\varepsilon_{SAM}} + \frac{\mu_{Metal/SAM}}{\varepsilon_{Metal/SAM}}$$
(26)

where ε_{SAM} and $\varepsilon_{Metal/SAM}$ represent the permittivity of the SAM and of the layer of atoms bonding the metal and the SAM, respectively.^[148] Tighter SAM packing allows for more dipole molecules per unit area that will contribute to the shift. For instance, the SAMs TP and 3-MFBT pack in a tighter c(6x2) arrangement than the p(2x2) configuration PFBT when
deposited on a Cu(100) surface.^[178] Consequently, TP gives a greater magnitude ΔWF than PFBT (0.94 eV vs 0.80 eV), even though PFBT has a stronger dipole moment. The same packing trend holds for the Au(111) surface where there is one TP molecule per 32 $Å^2$ vs one molecule per 85 Å² for PFBT.^[179] SAMs based on smaller molecules, such as the thiophenes, may be expected to have a lower degree of long-range order than longer SAM molecules (such as PFDT), due to the strength of intermolecular bonding.^[149] However, long-range order is possible with the right preparation conditions: Kang et al. created well-ordered PFBT superlattices on gold substrates by tuning the substrate temperature, PFBT solution concentration, and time of treatment.^[180] They noted that room temperature deposition was not favorable for long-range order, and that dilute (0.02 mM) or concentrated (50 mM) PFBT solutions never formed ordered domains. Substrate preparation can largely influence PFBT formation as well. For example, reducing the deposition rate of gold contacts increases the metal grain size, which results in improved injection, lower contact resistance, and enhanced device mobility.^[55] KPFM measurements detected localized areas of high work function shifts - "hot-spots" - leading to the hypothesis that the larger gold grains induced better PFBT ordering. Ordering can be highly dependent on electrode material, too. Referring back to the work discussed in Section 4.1,^[149] Kim et al. studied PFBT formation and function on gold, silver, and copper electrodes for pentacene-based OFETs. In contrast to other works, here PFBT only shifted the work function of the gold electrodes by 0.01 eV, attributed to poor PFBT ordering. However, with the same deposition procedure, PFBT shifted the work function of silver and copper contacts by 0.18 eV and 0.23 eV, respectively. The SAM treatment boosted drain currents for copper devices by nearly 4 orders of magnitude, and OFET mobility was on par with those of treated gold and silver devices (and better than the non-treated gold and silver devices). The gold devices still showed significant improvement, but since there was little work function shift, this was attributed to microstructure changes in the pentacene near the contacts.

A challenging aspect of adopting SAM treatment for work function tuning is that their presence also modifies the surface energy and chemistry, thus sometimes leading to changes in the microstructure of the semiconductor film, which can have a profound impact on contact resistance, channel resistance and overall device performance. [34,73,149,157,166,171,181,182] A wellstudied type of SAM-mediated microstructure change is that resulting from interactions between fluorinated SAMs and polyacene-based molecules. For example, the small molecule diF-TES-ADT contains fluorine and sulfur atoms at the each end of the acene chain that interact with fluorine sites on PFBT.^[73,157,166,181,183] This induces diF-TES-ADT crystallization in large grains where the molecules align almost exclusively in the "edge-on" orientation, while solutions deposited on untreated gold contacts form smaller crystals of mixed "edgeon" and "face-on" orientations, Figure 14.^[157,166,183] "Edge-on" crystals have the conjugated backbone perpendicular to the surface, which leaves overlapping π -orbitals extending parallel to the channel. Therefore, not only does the SAM create higher electrode work function, and larger crystal domains, but it induces ordering that aligns the high-mobility crystal direction with the plane of the channel. Analogous results have been obtained when this organic semiconductor was deposited on electrodes treated with TFBT or TTFP.^[171] Kim et al. showed that a low carrier density zone in the semiconductor near the contact interface makes a large contribution to contact resistance in coplanar devices.^[184] Increasing semiconductor mobility in this region through better molecular ordering helps relieve the constraint.^[149,184] Additionally, SAMs can buffer the semiconductor from the surface energy of the electrode, which improves wettability and reduces the number of gaps between the channel and the contact.^[13] This is even more critical for coplanar devices since the injection area is much smaller than that of staggered devices.

4.3 Doping

Doping has been critical to the performance and adaptability of modern inorganic semiconductors and holds the same promise for organic electronics. However, organic semiconductors bring new challenges. Weak van der Waals bonding in organic solids enable dopants to diffuse through the bulk, making the task of controlling the concentration and distribution of dopants very difficult – especially at interfaces. Diffused dopants alter the material properties much more than in substituted dopants for inorganic semiconductors. In addition, since organic semiconductors have a lower charge density than their inorganic counterparts, they also need to be doped at higher concentrations, complicating matters further. Dopants present in the channel, originating from either diffusion or bulk doping of the semiconductor, create a prominent issue: while the free-charge generation of channel dopants increases mobility, they often dramatically increase the off-current, too. Despite these challenges, doping has been used to tune and improve nearly every aspect of OFET operation including mobility,^[156,186,187] charge trapping,^[188,189] threshold voltage,^[63,190,191] stability,^[192,193] and injection.^[36,38,43,56,63,98,165,190,191,194-204]

Common p-type dopants for organic semiconductors include F4TCNQ,^[56,203,205–208] F6TCNNQ,^[63,190,206,209] and metal-halogens like FeCl₃^[36,38] and CuI.^[200] Doping has also been successful for creating stable n-type devices, with such dopants as rhodocene dimer,^[43] cobaltocene,^[210] (RuCp*Mes)₂ dimer,^[204,211] and the Lewis acids TBAF and TBAOH.^[194] For reviews on doping in OFETs, the reader is directed to the works by Lüssem et al.^[195] and Xu et al.^[196]

Doping the semiconductor itself raises its conductivity, thus reducing R_{ch} , but also $R_{C,bulk}$ in staggered-structure devices. As for the changes in $R_{C,int}$, dopants at the contact/semiconductor interface cause numerous effects that reduce both the height and width of the injection barrier.^[38,195,196,203] Organic semiconductors have a small charge density, and so they form large depletion zones when they are brought into contact with metals – a large

region of the semiconductor must contribute to charge transfer in order to establish thermodynamic equilibrium. The thickness of this depletion zone coincides with the thickness of the injection barrier. Dopants increase the charge density of the material, alleviating the demand on the semiconductor by providing free charges for exchange. This thins the depletion zone and promotes injection by tunneling (i.e., field emission).^[203] However, since tunneling current decays exponentially with tunneling distance, increasing the thickness of the dopant layer can have a negative effect on device performance. Hou et al. fabricated BGTC pentacene devices with F6TCNNQ dopant layers of various thicknesses (1 nm, 5 nm, and 10 nm) at the surface of the contacts and found that performance fell off quickly with increasing dopant thickness and the thinnest layer yielded the best performance.^[63] Injection efficiency is also modified by temperature, which alters the degree of charge transfer taking place between the dopant and the semiconductor.^[98] The charge exchange is reduced or suppressed at low temperatures, and indeed a shift to non-ohmic injection when cooling doped devices has been observed.^[63] Careful selection of dopants can reduce the height of the injection barrier by providing intermediate states between the metal and the semiconductor. Additionally, dopants can generate charge transfer complexes that fill traps, resulting in a higher effective carrier density.^[38] Finally, the interface dipoles formed between the dopant and the contact will shift the work function, potentially lowering the barrier.^[201]

There are a few efficient methods of doping the charge injection site. Bulk doping of the semiconductor, through solution or co-evaporation, stimulates effective charge transfer at the contact-semiconductor interface and has been shown to reduce contact resistance.^[194,197,204] Instead of doping the entire semiconductor, selectively doping targeted areas can offer better control of device properties. **Figure 16** shows an example of both strategies, as compared to the reference, an undoped OFET.^[198] Strategies to dope the contact include the use of self-assembled monolayers,^[199] photolithography,^[63] and shadowmask deposition.^[36,43,165,190,200,203] Self-assembled monolayer doping is only applicable for bottom-

contact OFETs, while photolithography and shadowmask deposition can be used with both bottom- and top-contact geometries. Top-contact depositions can improve performance by allowing dopants to diffuse into the bulk near the contacts, lowering $R_{C,Bulk}$. The top-contact shadow mask strategy was recently used by Yamamura et al. to achieve a contact resistance of 46.9 Ω cm in BGTC layered-crystalline OFETs.^[56]

Kim et al. have taken advantage of diffusion to selectively dope the contact area in poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) transistors.^[203] They employed a post-deposition doping technique where F₄TCNQ was deposited on the PBTTT films above the contact area in bottom-gate, bottom contact devices.^[203] The F₄TCNQ diffused through the top of PBTTT and down into the contact area. The device was etched in argon plasma for one second to passivate the more mobile neutral dopants, freezing in the diffusion and retaining the on/off ratios of untreated devices.^[203]

An efficient method for contact-only doping is to combine a dopant with a SAM. Nicht et al. functionalized F₄TCNQ with sulfur-containing triazole groups to create a dopant that selectively bonds with gold.^[199] To create the monolayer, the gold contacts were placed in a tetrahydrofuran solution containing F₄TCNQ and triazole disulfide. Pentacene transistors fabricated with these contacts exhibited an increase in mobility by factors of 3 and 1.5 compared to transistors with untreated gold and PFBT-treated gold contacts, respectively. Notably, on/off ratios also improved with the F₄TCNQ-triazole-SAM.

A serious issue with n-type transistors is the air-stability of both the semiconductor and the contact. Doping can help alleviate this problem. Wang et al. used the dimer $(RuCp*Mes)_2$ to bulk dope P(NDI-DPP) and create a robust n-type transistor with contact resistance of 53 M Ω (for reference, the undoped FET had a contact resistance of 419 M Ω).^[204] Singh et al. selectively doped the contacts of a C₆₀-based transistor with rhodacene dimer to lower the contact resistance from 9.7 k Ω cm to 5.5 k Ω cm, and they observed a corresponding increase device mobility from 0.48 cm²V⁻¹s⁻¹ to 1.65 cm²V⁻¹s⁻¹. The doped contacts also

reduced the dependence of R_C on V_{GS} , suggesting that doping can relieve the effects of a gated contacts. Zhou et al. created stable low work function electrodes using treatments with polymers containing aliphatic amine groups.^[202] The polymer is physabsorbed on the surface and the neutral amine group undergoes a charge transfer interaction with the host. The work functions of a variety of substrates has been reduced using this approach, including metals, metal oxides, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), and graphene. Treated contacts made from gold, silver, and aluminum had resulting work functions of 3.9 eV, 3.7 eV, and 2.75 eV, making this universal strategy for creating n-type devices. While contact resistance values were not reported, TGBC OFETs based on N2200 showed an improvement in mobility from 0.04 cm²V⁻¹s⁻¹ to 0.1 cm²V⁻¹s⁻¹ and a reduction in threshold voltage from 4.5 V to 0.4 V with treated gold contacts. Even when the polymer was deposited before the electrode in at BGTC configuration, IGZO-based transistors showed an increase in mobility from 0.004 cm²V⁻¹s⁻¹ to 1.2 cm²V⁻¹s⁻¹ and a drop in threshold voltage from 39 V to 1.5 V.

4.4 Oxides

Metal-oxides have been employed to reduce contact resistance in organic devices since at least 1996 when Tokito et al. found that thin films of molybdenum oxide, vanadium oxide, and ruthenium oxide reduced the work function of the contact and consequently boosted the efficiency of their devices.^[212] Since then, oxides of copper,^[213] nickel,^[214] titanium,^[215] and tungsten^[216] have all been employed as interlayers. The mechanisms by which oxides enhance charge injection is still the subject of research, with the work function tuning and charge transfer effects proposed as possible causes.^[11,12,28,165,217–219] Metal oxides have a wide range of work functions, from the 3.5 eV of zirconium oxide with a controlled density of defects to the 7.0 eV of vanadium oxide, making them extremely versatile interlayers for controlling charge injection into organic semiconductors.^[220] One example is the semiconductor C₈-

BTBT: with a HOMO level of around 5.7 eV, it introduces a large injection barrier for Au contacts ($WF \sim 5$ eV). The insertion of an MoO₃ interlayer reduced the contact resistance in C₈-BTBT devices by an order of magnitude from $\sim 10^5 \Omega$ cm for untreated Au contacts (which was expected due to the large injection barrier) to $\sim 10^4 \Omega$ cm for Au/MoO₃ contacts.^[221] In addition, the devices with oxide contacts showed a less pronounced gate dependence for contact resistance, evidence of a reduced Schottky barrier. The oxide layer also reduced the interface capacitance, improving the subthreshold swing from 1.3 V/dec to 0.22 V/dec. Other examples include vanadium oxide (V₂O₅, $WF \sim 7.0$ eV), which was used to increase the work function of molybdenum from 4.3 eV to 4.9 eV;[222] transistors based on P3HT and PC12TVT12T with Mo/V₂O₅ contacts had comparable performance to those with Au contacts, with the added advantage of reduced cost. Long et al. devised a method to deposit V2O5 from solution and were able to tune the work function of Mo from 4.45 eV to 4.85 eV by varying the solution concentration,^[218] and a similar method was applied to MoO₃.^[223] Darmawan et al. studied a variety of oxide films - including oxides of Al, Hf, Zr, Ta, Ti, and Si – and their effectiveness at improving pentacene devices when used as a 1 nm interlayer.^[224] Aluminum oxide (Al₂O₃) yielded the lowest contact resistance and the highest device mobility, with $R_c = 1.9 \text{ k}\Omega \text{cm}$ and $\mu = 0.52 \text{ cm}^2/\text{V}^{-1}\text{s}^{-1}$, compared to $R_c = 19.9 \text{ k}\Omega \text{cm}$ and $\mu = 0.32 \text{ cm}^2/\text{V}^{-1}\text{s}^{-1}$ for control devices with gold contacts. The work function of their Al₂O₃ films was measured to be 5.23 eV, which compares favorably to the measured pentacene HOMO of 5.19 eV. However, the interface dipole between Al₂O₃ and pentacene shifts the vacuum level by 0.28 eV, which leaves an injection barrier of 0.25 eV. This was still favorable to the 1.16 eV barrier found with gold contacts. Kumantani et al. found that pentacene devices with aluminum contacts exposed to air (forming Al₂O₃) outperformed devices with gold contacts and had a lower contact resistance.^[41] Silver oxide can be formed through UV-ozone treatment, and Minagawa et al. were able to boost the work function of silver contacts to 6.3 eV.^[225] They used these contacts to reduce R_c in pentacene transistors to

8.1 k Ω cm, compared to 46 k Ω cm with gold contacts and 25 k Ω cm for gold contacts treated with a MoO₃ layer.

Molybdenum(VI)oxide is one of the most studied oxides for OFETs. The work functions for molybdenum oxides are much higher than that of the pure Mo metal: Mo has a work function of 4.4 eV while MoO₂ and MoO₃ have work functions of 5.9 eV and 6.7 eV, respectively.^[217,219,220] These values correspond to samples prepared either through *in-situ* metal oxidation or sublimation. However, MoO₃ layers have been reported to have work functions between 5.2 eV and 5.8 eV, for instance when exposed to air or deposited on gold.^[28,165,226–231] The discrepancy can arise from the thickness of the layer, reactions with the substrate, or environmental effects. Gwinner et al. studied the depreciation of MoO₃ contacts and determined that the work function declined from 6.7 eV to 5.2 eV, even in a nitrogen glovebox.^[219] Since the depreciation was found to occur much faster in ambient atmosphere, but slower in dry air, it was suggested that water was the cause of work function shift. Further investigation with XPS revealed that water absorption disrupted clusters of MoO₃, but the oxide did not react with the water. The devices could be rejuvenated by annealing at ~120 °C in a nitrogen glovebox.

Although metal-oxides have been proven to enhance charge injection, tradeoffs exist. Many oxides are insulating, and so there is a balance involving the thickness of the oxide and the conductivity. A thin oxide layer allows for efficient tunneling, but unfortunately the work function of the oxide decreases as the film gets thinner.^[232] This is due to multiple causes, including inadequate screening of the underlying substrate material, reactions with the substrate material, and dimensional confinement. MoO₃ tends to oxidize contacts; for instance, when MoO₃ is placed on nickel, the molybdenum will be reduced to Mo⁵⁺ close to the contact.^[220] This reduction extends several nanometers, lowering the work function for any films of that thickness.^[220] The same is true if MoO₃ is placed on pure molybdenum, and vanadium substrates will further reduce the molybdenum into Mo⁴⁺. Even when paired with a

much less reactive metal like gold, Mo^{5+} can still form, possibly through a charge-transfer interaction.^[220] However, deposition of MoO₃ on comparatively unreactive gold decreases the required thickness for work function saturation. For example, MoO₃ on Au exhibits a work function of 6 eV at a thickness of 0.28 nm, while it takes 0.85 nm of MoO₃ to achieve the same work function on a molybdenum substrate. Note that depositing MoO₃ on copper forms a Cu-Mo-O alloy and pins the work function at $\approx 6 \text{ eV}$.^[232] To summarize, as the oxide film thickness increases, the work function increases, but conductivity decreases (excluding intrinsically conducting metallic oxides). Significant effort has been dedicated to optimizing oxide thickness to find a good balance between the two and minimize contact resistance in OFETs. The exact optimal thickness depends on the nature of the other layers within the device (contact, substrate, semiconductor), as well as its geometry.^[28,233]

The physics behind the function of oxide interlayers can be complex. As demonstrated, the primary contribution to function seems to be a better alignment between work function and the HOMO or LUMO of the semiconductor. However, there are more effects and subtleties; for instance, studies have found evidence that MoO3 acts as a p-type dopant.^[41,165,219] In 2016, Choi et al. performed an experiment comparing three different interlayers on Au contacts: PFBT, MoO3, and molybdenum tris-[1,2-bis(trifluoromethyl)ethane-1,2-dithiolene] (Mo(tfd)₃).^[165] Both molybdenum-based layers outperformed the Au and Au/PFBT contacts, but more interestingly there was no correlation between work function and contact resistance. When examining the work function of the electrode, they found that it was pinned at 4.89 eV. This Fermi pinning explained why the increased work function of MoO3 vs. Mo(tfd)₃ had no significant effect on performance. Another important finding of the study was the effect that the oxides had on bulk resistance in staggered transistors. $R_{C,int}$ was found to be negligible for all the devices with work functions above the pinned Fermi level (i.e., all but bare Au), but $R_{C,bulk}$ was severely reduced in samples with molybdenum interlayers. In other words, the principal effect of the oxide was

not to reduce the interface resistance, but rather the bulk resistance. Since there was no evidence of diffusion of MoO₃ or Mo(tfd)₃ into the semiconductor, it was suggested that a long-range charge transfer resulting in p-type doping occurred. This effect was stronger with Mo(tfd)₃ interlayers and resulted in better OFET performance.

Most contact-tuning strategies rely on adding a single material between the electrode and the semiconductor, but Kotadiya et al. have developed a widely applicable strategy that incorporates two interlayers.^[234] The first layer is a high-work function oxide, such as MoO₃, WO₃, or V₂O₅. The second interlayer is an organic semiconductor, and the only requirement is that it has an ionization energy (IE) larger than the HOMO of charge transport region. The evidence suggests that this second interlayer effectively decouples the semiconductor from the rest of the contact, eliminating the Schottky barrier and creating an ohmic contact. Test devices sandwiching tris(4-carbazoyl-9-ylphenyl)amine (TCTA, IE = 5.7 eV) between a PEDOT:PSS electrode and a double-layer electrode showed improved injection for a variety of organic interlayers on MoO₃, including 4,4' -bis(N-carbazolyl)biphenyl (CBP, IE = 6.0eV), 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN, IE = 6.1 eV), C_{60} (IE = 6.4eV), and 4,4' ' -bis(triphenylsilanyl)-(1,1',4',1'')-terphenyl (BST, IE = 7.0 eV). The same trend was observed when CBP was used as the active material, even though it has a large IE of 6.0 eV: C₆₀, 4CzIPN, and BST improved performance, while TCTA, with an IE less than that of CBP, reduced performance. The improvement trend held for several other combinations of semiconductors and oxides, suggesting that this strategy can be applied to a variety of devices. Another recently developed bilayer structure incorporates a polycrystalline semiconductor in between a metal electrode and the alkane tetratetracontane (TTC), i.e., a metal/OSC/TTC contact.^[235] This method allowed for enhanced hole and electron injection. Not only did the bilayer contact improve hole injection when used with gold electrodes, but it improved hole injection from calcium electrodes to beyond that of bare gold. Similarly, the

bilayer contact improved electron injection from gold electrodes to beyond that of calcium. These phenomena were attributed to creating an injection pathway where carriers hop through states in the band gap.

4.5 Organic Electrodes for OFETs

So far, we focused on OFET devices with source and drain electrodes consisting of inorganic metals or chemically tailored metallic electrodes. Organic metals have gained attention as alternatives to conventional metals due to their low-cost processing and better interface morphology that they can yield given the similarities in composition, hence better compatibility with the organic semiconductor. They include charge transfer complexes (CTs),^[161,236-240] PEDOT-derivatives,^[241-247] carbon nanotubes (CNTs),^[248-253] graphene and its derivatives.^[243,254–262] For example, dibenzotetrathiafulvalene OFETs with contacts consisting of tetrathiafulvalene - 7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ) (Figure 17a) yielded significantly lower contact resistance and higher mobility than those with Au contacts, in spite of a higher Schottky barrier estimated from the value of the work functions. This behavior was attributed to a smaller potential shift at the organic/organic interface compared to the inorganic/organic interface.^[263] The CTs are donor:acceptor crystals, which are typically grown by evaporation methods due to their low solubility (co-evaporation or evaporation of the solution-grown complex), and the nature of the constituents, the stoichiometry, the degree of charge transfer between the donor and acceptor, and solid state packing of the resulting co-crystal dictate their electronic properties.^[161,264,265] Several solution-based processing methods have been developed for the deposition of organic metals based on CTs, including double shot ink-jet printing,^[266] subsequent deposition from capillaries,^[267] and dispersing from a nanoparticle solution.^[268] TTF-TCNQ is the most common organic metal, and it has been used as electrodes in both p-type and n-type OFETs of various TTF derivatives,^[239,263] pentacene,^[238,240] copper-phtalocianyne,^[238] DBTTF-

TCNQ,^[237] and fluorinated copper-phtalocianyne.^[269] Selective deposition of TCNQ over the organic semiconductor tetramethyltetrathiafulvalene (TMTTF) or hexamethylenetetrathiafulvalene (HMTTF), led to inter-diffusion and "on the spot" mixing between the two species, leading to the formation of the organic electrode in self-contact transistors.^[239,270] These devices produced the lowest contact resistance ($R_CW = 80$ k Ω cm) compared to Au ($R_CW = 3600$ k Ω cm), and even the organic metal TTF-TCNQ, when this was used as a stand-alone contact ($R_CW = 200$ k Ω cm) (Figure 17b), and the devices with organic electrodes outperformed those with Au in all experiments.

We limited our discussion to several examples based on CTs; a review on charge transfer complexes was recently published by Goetz et al.,^[271] and one dedicated specifically to OFET electrodes consisting of these materials by Pfattner et al.^[236]

Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is a very popular organic electrode for hole injection ($WF \approx 5 \text{eV}$) due to its compatibility with solution processing, which makes its manufacturing relatively simple and scalable. This material was incorporated in OFETs both as an interlayer,^[245] and a stand-alone electrode.^[241–244] A similar compound (PEDOT:Tos), with Tos = tosylate, served as electron injector (WF = 4.3 eV).^[246] More examples for this type of electrode are provided in Section 5. A drawback of these materials is their low conductivity and fast degradation in the presence of moisture. A solution for the conductivity challenge is to blend them with multi-wall nanotubes.^[247]

CNTs have also been explored as contacts for OFETs, both as single walled (SWCNTs),^[248–251] and multi-walled (MWCNTs) nanotubes.^[253] In addition to ease of processing, high work function (\approx 4.8 eV to 5 eV) and high electrical conductivity, these systems exhibit a one-dimensional (1D) structure, which could induce strong electrostatic effects at the interface with the organic semiconductor, thus possibly facilitating charge carrier tunneling across the contact Schottky barriers.^[252] Ciccoira et al. found contact resistance values in the order of $R_C \approx 200 \text{ k}\Omega$ in phenyl-C61-butyric acid methyl ester

(PCBM) transistors with CNT electrodes, compared to greater than 1 M Ω in similar devices, but with Au contact.^[249]

Another contact type is based on graphene and its derivatives (such as reduced graphene oxide -RGO), which was adopted for several proof-of-concept OFETs, including pand n-type, solution and vacuum deposited organic semiconductor layers.^[243,254–262] Interestingly, it was found that RGO contacts yield lower contact resistance than Au contacts, in spite of their lower conductivity, similar to the case of CTs.^[259] Such contact presents an additional advantage of being transparent, therefore it was widely adopted in solar cell and organic light emitting diode fabrication.^[254] Although not many details about contact resistances in OFETs with graphene electrodes are provided, in general the devices with such contacts outperform those with Au contacts, suggesting that this can be a viable option for fabrication of electrodes in OFETs.

5. Printed contacts in OFET devices

One of the key advantages of organic semiconductors is their compatibility with printing techniques.^[272–275] To fully take advantage of this feature towards the development of low-cost (opto-)electronic devices, the materials and processing necessary for the other device layers must offer the same opportunities. Extensive effort is aimed towards the development of dielectric and electrode materials compatible with solution deposition, or other cost-effective processing methods. In this section we will review recent reports focused on OFET electrodes fabricated using printing techniques. Printing can be used for both deposition and patterning of the electrodes and could allow the realization of "all printed", low-cost OFETs on flexible substrates.

Solution deposited contacts include PEDOT:PSS^[276,277], graphene and graphene oxide^[277,278], organic charge transfer complexes^[266,279], carbon nanotubes^[280], and metal nanoparticles^[281,282]. Printing is a scalable, inexpensive, and energy efficient technique that

can be used to create electronics on flexible substrates and allows for customizable applications with similar opportunities in small scale electronic design that 3D printing has had in manufacturing.^[283] Methods under development for printed electronics include inkjet, spray, gravure, flexographic, and screen printing. Progress in developing printed electronics can be found in several reviews.^[284-287] Common metallic materials used for solvent based printing are nanoparticles dispersed in organic solutions, which often are sintered at temperatures above 100°C or by laser heating to remove ligands and increase conductivity.^[274] Materials available for printed metallic components are usually set by the ability to solvent print these materials with low resistivity and high resolution, and therefore options to develop and improve contact resistance are more limited. Fukuda et al. report contact resistance in OFETs as low as 1.8 kΩcm for inkjet printed silver nanoparticle inks treated with a SAM layer^[47] and by adding gold nanoparticles to a silver ink Teng et al. were able to reduce ϕ_B from 1.5 eV to 1 eV.^[282] Kostianovskii et al. developed solution processed contacts using patterned PEDOT:PSS with $R_C = 0.98$ k Ω cm in OFETs made with a copolymer of 1,4-diketopyrrolo[3,4-c]pyrrole (DPP) and thieno[3,2-b]thiophene moieties (DPPT-TT)^[288].

Printing electrode materials in succession for the additive manufacturing of printed electronics necessarily requires consideration of each layer with respect to the surface energy, solvent and printing properties of the next. The size and shape of contacts printed can result in uneven surfaces and the "coffee-ring" effect where material consolidates at the edge of a printed drop, impacting the printing of subsequent layers.^[289] Therefore, controlled solvent quality^[276] and drying conditions^[281,289,290] have been developed to improve printed morphology of contacts. Printed contact resolution is limited by the ability to control the shape of the printed feature; methods to improve resolution are covered in the review by Tang et al.^[285] Using a pattern of hydrophobic and hydrophilic surfaces, following a self-aligning

technique,^[291] Pierre et al. were able to control the patterning of blade-coated PEDOT:PSS contacts.^[276] Decreasing nozzle and droplet size has led to short channel transistors without further processing, down to $L = 9 \ \mu m$ for inkjet printing^[292] and $L = 1 \ \mu m$ for systems that use electric pulses to create femtoliter volumes of ink, **Figure 18a**.^[293]

Contact processing can be damaging to organic semiconductor layers, and so bottom contact devices are common. Bottom contacts can create a problem in which the dielectric and contact interfaces have different surface energies, which results in uneven crystallization across the device when a solution processed semiconductor is printed on top. To relieve the issues of energetic mismatch and surface energy mismatch, SAMs are used on both the contacts and the dielectric to enhance the semiconductor adhesion and reduce contact resistance.^[281,295] Research done by the Hong group has developed a method in which a thin layer (≈ 4 nm) of dimethylchlorosilane-terminated polystyrene (PS-Si(CH3)2Cl) is applied to the entire device before semiconductor layers across the device for Ag-nanoparticle^[296] and PEDOT:PSS contacts.^[297]

Inkjet printing allows for simultaneous deposition and patterning of device electrodes. Other methods for low-cost electrode patterning include the use of fluorine based orthogonal solvents, which was pioneered by Malliaras and collaborators.^[298,299] Recently, Harper et al. developed aerosol spray lithography, a method which relies on patterning OFET electrodes with a digitally printed mask using a laser printer, and depositing contacts by aerosol spray (Figure 18b).^[294] The technique is effective for both top and bottom contact devices, as well as several combinations of organic semiconductor/electrode materials. The contact resistance was quite large, $R_C = 2 \text{ M}\Omega\text{cm}$, and the resolution defined by the resolution of the printer used for contact definition was approximately 70 µm.

Improvements to R_C for printed contacts are naturally expected to lag behind conventional methods due to requirements to optimize material printing and contact resistance

simultaneously. Lowest reported contact resistances in printed devices are therefore still above lowest values reported in Table 1 and Figure 1 (on the order of several k Ω cm^[47,281,293]). Further development of new materials and device architectures will likely expand the library of electrode materials and processing methods to combine high performance with the cost effectiveness and customizable circuit design offered by printing methods.

6. Future Perspective

In this review, we outlined the fundamental physics governing charge injection in organic semiconductors, and OFETs in particular, we described several methods for contact resistance measurement, and strategies being implemented to reduce contact resistance and improve OFET functionality. We provided a summary of the lowest reported contact resistance as a function of time and highlighted the fact that a fast and significant progress has been witnessed in the last 5-7 years. Nevertheless, the contact resistance remains over four orders of magnitude higher than the lowest obtained in inorganic FETs.^[18] The main difference comes from the fact that charge injection into inorganic semiconductors relies on bulk/near surface doping, and the dopants are usually substitutional, not interstitial. A density of activated charge carriers greater than 10^{19} cm⁻³ is typically needed to compress the depletion region associated with the Schottky barrier formed at the metal-semiconductor interface such that tunneling becomes an efficient injection process. Perhaps it is not coincidental that the fully accumulated channel density (ca. 10^{19} cm⁻³) can also compresses the barrier for OTFTs limited by large Shottky barriers and give rise to the often cited "kink" in the ID-VGS characteristics, a signature of the transition from contact controlled transconductance to channel controlled transconductance. But in general, such substitutional doping in not possible with molecular systems bound by weak van der Waals forces and having limited frontier orbital overlap. Here, dopants are interstitial and the doping density needed to adequately compress the depletion region can greatly perturb the electronic structure and

transport properties, often in unpredictable ways, and even giving rise to a solid state system which no longer shares the physical properties, of the semiconductor system before doping. Organic semiconductors are unique in that fully dressed charge carriers relax (thermalize) from the energy level associated with injection. The interaction with the molecular framework and low permittivity compared to inorganic semiconductors result in relatively large shifts in energy (e.g. molecular polarons are typically 100 meV to 150 meV from molecular levels (EA and IP) widely viewed to be commensurate to the conduction and valence bands). The polarizability and low permittivity can also give rise to large shifts in critical energy levels at the surface that are difficult to predict when measured in vacuum vs. against another organic semiconductor vs. against a metal (or metal oxide that provides some screening to the electrons in the metal). It is only within the last 10 years that the community has more widely appreciated the differences between OLEDs, OPVs, and OTFTs, i.e. that the charge carrier density (injected and transported) differs and that the 1-D injection and transport models applied to OLEDs and OPVs do not adequately capture the physics that govern OTFTs. As highlighted in this review, injection and transport levels remain largely associated with molecular levels (EA and IP) - this may not be very accurate despite its wide adoption and occasional utility as a working model. In OLEDs, (we'll imply here that OPVs remain a special case where the requirements for efficient charge extraction should not be viewed or described in the same way as charge injection), a broad distribution of states is assessable to inject charge, the electric field is 10x larger (approaching 1 MV/cm), the carrier concentration is much lower than in OTFTs, and charge transport occurs via hopping with a dominant energy for the transported carriers far removed from molecular levels and shifted modestly from the demarcation between occupied and unoccupied tail states. In OTFTs, the in gap state distribution is sharp (smaller tail state slope and in gap density) and the charge carrier accumulation in the channel pushes the Fermi-level close to the often referenced molecular levels (near the band edge). Hence, our overall view of energy level alignment

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may not be as well understood as previously thought, e.g. injection from the metal Fermi-level into unoccupied states vs. into a molecular level (IE or EA).

Further improvement of R_C in OFETs is on the immediate horizon and will require continued effort. Measurement science, modeling, and mitigation strategies are codeveloping, forming a feedback loop to drive device improvement. The traditional measurement methods, such as gTLM and four-point probe, have been modified to include factors that will accommodate novel materials with bias dependent mobilities and contact resistances. Modeling is being enhanced to include sources of non-linearities and corrections that apply to non-traditional semiconductors, such as edge states. In return, methods to improve contact resistance are directed: the most promising candidates to improvement are being demonstrated though modifying the barrier with SAMs, oxides, and doping, and improvement to OFET design.

Most of the studies included in this review have focused on the goal of reducing contact resistance to a negligible factor in device performance. While this will benefit many applications, recent work has also highlighted the opportunities for contact dominated devices or in blocking contacts for unipolar devices. Schottky barrier transistors are considered for large gain devices which take advantage of large, non-linear contact resistance. The intrinsic gain of these devices are estimated at 1100 for an OFET consisting of C8-BTBT.^[300] These devices use very low current and voltage as they are run in the subthreshold regime where the exponential dependence of the Schottky-barrier resistance dominates. Fernandez and Zojer showed that careful design of a Schottky contact barrier may aid in decreasing off-current in short channel devices, which may enhance the performance provided that this is balanced with the on-voltage of the device.^[301] Similar to light emitting diodes and photovoltaics, high resistance blocking contacts can be used in OFETs to control charge type and recombination within the device and has been used to improve n-type transport in transistors that use ambipolar materials.^[154]

While the work to improve contact resistance is expanding, there remain several areas that would benefit from further study. In the end of this review, we will include some recommendation for further progress in minimizing contact effects in organic devices. Measurements that focus on current injection are lacking, hindering the development of implementable models. Effort focused in this area is therefore urgently needed in order to advance the device design in a rational way. Consistent and accurate reporting of contact resistance is crucial to device improvement, and we encourage further studies, especially those dedicated to material development, to include R_C reporting as a standard figure of merit alongside semiconductor parameterization. We emphasize the fact that contact resistance in OFETs is a very convoluted parameter, which depends not only on the nature of the electrode and organic semiconductor materials, but also on the various phenomena taking place at this interface, the processing steps, and geometric parameters. Understanding of charge injection and transport phenomena has matured, which has resulted in steady improvements in device performance. Future improvement to the contact resistance in OFETs will benefit from drawing on the multiple techniques and advances in understanding of the injection interface, allowing these devices to reach their potential. We hope that this review, along with the recommendations included in it, will provide a guide into the physics of contact resistance and the related manufacturing steps, and help in creating new standard procedures for reporting device performance that will allow reliable comparison and faster progress.

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Figures



Figure 1. Selected lowest reported contact resistances in OFET devices for the past 20 years, between 1999 and 2019. The inset shows the structure of an OFET.



Figure 2. a) Linear transfer characteristics calculated for four different contact resistance cases: (i) $R_C < R_{ch}$ and R_C slowly decreases with gate bias (blue curve), (ii) $R_C > R_{ch}$ and R_C rapidly decreases to be $R_C < R_{ch}$ (red curve), (iii) $R_C > R_{ch}$ and R_C slowly decreases (pink curve), and (iv) $R_C = 0$ (black curve). Adapted with permission.^[57] Copyright (2017) American Physical Society. b) Saturation transfer characteristics for a rubrene single crystal transistor with gold contacts. Adapted with permission.^[58] Creative Commons Attribution 4.0 International License. c) Output characteristics measured for a pentacene thin-film transistor with one palladium and one nickel contact. The device was measured with Pd as the source (black) and Ni as the source (grey). Adapted from.^[59], with the permission of AIP Publishing.. d) Output characteristics of a 2,8-difluoro-5,11-bis (triethylsilylethynyl) anthradithiophene (diF-TES ADT) OFET device that does not reach saturation. Adapted with premission.^[60] Copyright (2008) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.



Figure 3. a) Energy levels of metal and organic semiconductor (OSC) before they are brought in contact or immediately after contact (before the equilibrium is established). b) After contact, alignment of the Fermi levels is established through exchange of charge. A depletion region with width d forms. Lines at the top and bottom of the frontier molecular orbitals represent energetic broadening of the states, purple lines indicate formation of interface states.



Figure 4. Injection of holes from a metal into an organic semiconductor: a) thermionic field emission, b) direct tunneling, c) Fowler-Nordheim tunneling, d) diffusion. Dashed arrow shows recombination.



Figure 5. The temperature and field dependence of charge injection for the pentacene/carbon nanotube interface. Region I corresponds to thermionic behavior, region II follows direct tunneling, and region III is Fowler-Nordheim tunneling. Reprinted with permission.^[68] Copyright (2012) American Chemical Society.



Figure 6. a) Voltage profile of an ideal FET ($R_C = 0$). No voltage is dropped at the contacts, $\Delta V_{ch} = V_{app}$. b) Voltage profile showing a real FET ($R_C \neq 0$) with voltage drops at the source and drain, leading to $\Delta V_{ch} < V_{app}$, shown as a reduced slope. c) The total FET resistance is a sum of three resistances connected in series: the source, channel, and drain resistances (R_S , R_{ch} , and R_D , respectively).



Figure 7. Coplanar FETs. a) Bottom contact, bottom gate device. b) Top contact, top gate device. c) Image showing the electric fields generated by V_{DS} and V_{GS}, along with an orange arrow representing the total resulting field. In a coplanar device, the injected current, J_{int}, flows in the same direction as the device current. d) Equivalent circuit (simple model) of the OFET: the circuit elements, R_{C,int} and C_{int} represent the injection process and R_{ch} represents the resistance through the channel.



Figure 8. Staggered FETs. a) Top contact, bottom gate device. b) Bottom contact, top gate device. c) Electric fields generated by V_{DS} and V_{GS} . In a staggered device, the injected current, J_{int} , flows perpendicular to the device current, J_{FET} . d) Equivalent circuit (simple model) for the OFET: the circuit elements, $R_{C,int}$ and C_{int} , represent the injection process, $R_{C,bulk}$ is the resistance through the semiconductor below the contact, and R_{ch} represents the resistance through the channel.



Figure 9. Gate voltage dependence of the contact resistance in OFETs of staggered geometry, with treated contacts: molecules 1,3,4,5,7,8-hexafluorotetracyanonaphthaquinodimethane (F₆TNAP) and 2,3,5,6- tetrafluoro-7,7,8,8,-tetracyanoquinodimethane (F₄TCNQ) were used to modify the work function of the contact to the semiconductor (C₁₀-DNTT) for two different values of L_0 . a) A thin device ($L_0 = 15$ nm of semiconductor) where the effect of the injection barrier can be observed as a change in R_C with changing contact treatment. b) In the limit where the mobility through the bulk dominates ($L_0 = 45$ nm), the contact resistance for the two doped contact types becomes similar, while the gate voltage dependence remains. Lines show fitting to Equation 17. Reproduced with permission.^[90] Copyright 2016 IOP Publishing Ltd.



Channel Length Figure 10. Example of data showing a non-linear increase in total resistance with respect to length. Estimating R_C by extrapolating from R_{Tot} at longer channel lengths (red line) yields an artificially lower R_C value than when extrapolating from shorter channel lengths (blue line).



Figure 11. a) Potential profile of a polytriarylamine thin film transistor biased at $V_{GS} = -10$ V for several V_{DS} values. b) Electric field derived from data in (a). Reproduced with permission.^[51] Copyright 2016 AIP Publishing.



Figure 12. Output characteristics of BGTC pentacene OFETs with Au, Cu, Ni, and In contacts. Copper contacts compared well to gold contacts, although devices with copper and nickel contacts show "S-shape" behavior at low V_{DS} , evidence of significant R_C . Nickel and gold have very similar work functions, but devices with nickel contacts had severely reduced charge injection. Indium contacts proved to be an extremely poor choice for p-type injection into pentacene. Reproduced with permission.^[25] Copyright 2006 AIP Publishing.



Figure 13: Work function tuning with SAMs. a) Thiophenol (TP), with an upward-facing dipole, shifted the work function of silver close to the semiconductor LUMO and promoted n-type device operation, as seen in b). Pentafluorobenzene thiol (PFBT), with a downward-facing dipole, shifted the work function close to the semiconductor HOMO and promoted p-type operation, as seen in c). Adapted with permission.^[164] Copyright 2017, Nature Publishing Group. d) Work function tuning of gold using SAMs resulted in corresponding decreases in contact resistance in diF-TES-ADT OFETs. Reproduced with permission.^[171] Copyright Elsevier 2017. e) Mixing two SAMs with opposite dipoles facilitated controlled work function tuning, here on a gold surface. Adapted with permission.^[173] Copyright 2014, American Chemical Society.



Figure 14. SAM-induced ordering in the OSC layer. a) Optical micrograph of a dif-TES-ADT OTFT, with the OSC deposited on untreated gold. b) The diF-TES ADT forms small grains and adopts mixed orientations of "edge-on" and "face-on". c) Optical micrograph of a dif-TES-ADT OTFT, with the OSC deposited on PFBT treated gold. d) The diF-TES ADT forms large grains consisting of "edge-on" orientation. Panels a) and c) reproduced with permission.^[185] Copyright 2008 AIP Publishing.



Figure 15. Doping near the contact thins the depletion layer and improves injection by tunneling, reducing $R_{C,int}$. Dopants at the contact will also fill traps near the contact, reducing $R_{C,Bulk}$. Reproduced with permission.^[38] Copyright AIP Publishing 2012.



Figure 16. a) Undoped devices have high on-off ratios but show signs of significant contact resistance, as evidenced by the "S-shaped" output curves. b) A doping layer that forms an interface between the OSC and the electrodes as well as the OSC and dielectric reduces contact resistance and gives higher drain current but comes at the cost of high off-currents. c) A doping layer selectively placed at the contact/OSC interfaces provides low contact resistance and retains the low off currents comparable to the control. Reproduced with permission.^[198] Copyright 2011 John Wiley and Sons.



Figure 17. a) Crystalline packing of the organic metal TTF-TCNQ, showing a segregated stack of the donor (TTF) and acceptor (TCNQ) molecules. b) Contact resistance in tetramethyltetrathiafulvalene OFETs with Au, and CTs source and drain contacts. Reproduced with permission.^[270] Copyright 2013 AIP Publishing.



Figure 18. a) Inkjet printed Ag contacts with high resolution, reprinted with permission.^[293] Copyright (2008) National Academy of Sciences. b) Electrode patterning using laser printing: a printed mask (teal) uses regular toner; the electrods are deposited by spray deposition (gray). Adapted with permission.^[294] Creative Commons Attribution 4.0 International License.

Table 1.	Contact resistan	ce values	included i	n Figure	1, together	with the deta	ils about t	he
OFET str	ucture and comp	position.						

Year	<i>R_C</i> (Ωcm)	Semiconductor	Contact	Geometry	Reference
1999	8 x 10 ⁴	Sexithiophene	Au	Staggered	[19]
2000	5 x 10 ⁵	Sexithiophene	Au	Staggered	[20]
2002	8 x 10 ⁶	F8T2	Au	Coplanar	[21]
2003	6.2 x 10 ⁴	Pentacene	Au	Coplanar	[22]
2003	3.0 x 10 ⁴	Pentacene	Au	Staggered	[22]
2004	4.4 x 10 ⁴	PTCDI-C5	Au	Staggered	[23]
2004	3.5 x 10 ⁴	PTCDI-C5	Ag	Staggered	[23]
2004	1.2 x 10 ⁴	Pentacene	DNNSA- PANI/SWNT	Coplanar	[24]
2006	1.2 x 10 ⁴	Pentacene	Pd	Coplanar	[25]
2006	1.5 x 10 ⁴	Pentacene	Au	Coplanar	[25]
2006	1.2 x 10 ⁴	Pentacene	Au	Staggered	[25]
2007	1.8 x 10 ⁴	Pentacene	Au	Staggered	[26]
2007	2.3 x 10 ⁴	Pentacene	Au/F4TCNQ	Staggered	[27]
2008	2.4 x 10 ⁵	Pentacene	Au/MoOx	Staggered	[28]
2008	1.3 x 10 ⁵	РЗНТ	Au/PFBT	Coplanar	[29]
2009	9.9 x 10 ⁴	Pentacene	Ag	Coplanar	[30]
2009	4.7 x 10 ⁴	Pentacene	Ag	Staggered	[30]
2010	2.1 x 10 ⁴	TIPS- Pentacene	Au/PFDT	Staggered	[31]
2010	9.3 x 10 ⁴	N1400	Au/MeTP	Staggered	[31]
2010	2.0 x 10 ⁵	TFB	Au/PFOT	Staggered	[31]
2010	1.0 x 10 ⁴	dif-TES-ADT	Au/PFBT	Staggered	[32]
2011	1.8 x 10 ⁵	P3HT	Au/BTFMBT	Coplanar	[33]
2011	4.5 x 10 ⁴	pBTTT	Au/PFDT	Staggered	[34]

2011	1.1 x 10 ⁵	Pentacene	Au	Coplanar	[35]
2012	1.0 x 10 ²	C ₈ -BTBT	Au/FeCl ₃	Coplanar*	[36]
2012	3.1 x 10 ⁴	PDI-8CN2	Au/ 4- chlorobenzene- methanethiol	Coplanar	[37]
2012	8.8 x 10 ³	C ₈ -BTBT	Au/FeCl ₃	Staggered	[38]
2012	6.0 x 10 ²	DNTT	Au	Staggered	[39]
2013	3.3 x 10 ²	C ₁₀ -DNTT	Au	Staggered	[40]
2013	1.6 x 10 ³	Pentacene	Au/Be	Staggered	[41]
2013	1.1 x 10 ²	C ₁₀ -DNTT	Au/F ₆ TNAP	Staggered	[42]
2013	5.5 x 10 ³	C ₆₀	Au/rhodocene dimer	Coplanar	[43]
2013	1.0 x 10 ⁴	C ₈ -BTBT	Au/FeCl ₃	Staggered	[44]
2014	1.1 x 10 ⁴	PDPP-TVT	Au	Staggered	[45]
2014	4.8 x 10 ²	C ₁₀ -DNTT	Au	Staggered	[46]
2014	1.8 x 10 ³	Lisicon [®] S1200	Au/Lisicon® M001	Coplanar	[47]
2015	3.0 x 10 ²	DPh-DNTT	Au	Staggered	[48]
2015	1.4 x 10 ³	Pentacene	Au	Staggered	[49]
2015	1.5 x 10 ³	Tetraceno [2,3- b]thiophene	Au	Staggered	[49]
2015	1.2 x 10 ²	C ₁₀ -DNTT	Au	Staggered	[50]
2015	1.3 x 10 ³	BASF GSID- 104031-1	Au/TTF	Staggered	[50]
2016	1.3 x 10 ²	DNTT	Au	Staggered	[51]
2016	2.0 x 10 ²	C ₁₀ -DNTT	Au	Staggered	[52]
2017	1.0 x 10 ²	C ₈ -BTBT	Au	Staggered	[53]
2018	4.2 x 10 ²	DNTT	Au	Staggered	[54]

2018	2.0 x 10 ²	IDTBT	Au/PFBT	Staggered	[55]
2018	5.0 x 10 ²	dif-TES-ADT	Au/PFBT	Staggered	[55]
2018	47	C ₈ -DNBDT-NW	Au/F4TCNQ	Staggered	[56]
2019	56	DPh-DNTT	Au	Staggered	[13]
2019	29	DPh-DNTT	Au/PFBT	Coplanar	[13]

ToC Text

This review focuses on charge injection in organic field-effect transistors (OFETs), with emphasis on the interplay between device performance (beyond mobility) and contact resistance. It summarizes the charge injection mechanisms in organic semiconductors in relation to OFET operation, provides an overview of measurements for evaluation of contact resistance, outlines recent progress in contact design, a historical overview and future perspectives.

Keywords: Organic Field-Effect Transistors, Contact Resistance, Organic Thin-Film Transistors, Charge Injection, Organic Semiconductors

Matthew Waldrip, Oana D. Jurchescu, * David J. Gundlach, and Emily G. Bittle*



