

Electrical Contacts to Molecular Layers by Nanotransfer Printing

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ABSTRACT

We introduce a novel approach, nanotransfer printing (nTP), to fabricate top-contact electrodes in Au/1,8-octanedithiol/GaAs junctions. Current–voltage and photoresponse experiments were conducted to evaluate the nature of electrical contact. Results show that the nTP method produces superior devices in which the electrical transport in nTP devices occurs through the 1,8-octanedithiol molecules. By contrast, conventional evaporation of Au onto the molecules results in direct Au/GaAs contacts. Thus, nTP is potentially useful for making electrical contacts in molecular electronics.

Organic molecules whose electronic properties can be specifically tailored and controlled through well-established synthetic chemistries are increasingly being targeted as active components in electronic devices. Technological advances in molecular-based electronics, however, remain limited because of the lack of understanding and control of the electrical contacts that form between electrically active organic components and inorganic electrodes.¹ Because of the mechanical and chemical fragility of the organic materials, establishing electrical contact with the organic component in a reliable fashion has been a major challenge. Here we introduce a technique, nanotransfer printing (nTP), for directly printing electrical contacts onto molecular layers at ambient conditions. Comparisons between nTP molecular junctions and junctions fabricated by conventional metal evaporation methods provide insight into how electrode fabrication affects electrical transport in molecular devices.

Presently, the top electrodes of most organic molecular devices are fabricated by the direct evaporation of metals onto the molecular layer. This approach generally results in extremely low yields of functional devices—they tend to be electrically shorted between the two electrodes across the molecules.² In an attempt to circumvent electrical shorts between contacts, nanoscale junctions,³ mercury droplets,⁴ lift-off float-on Au pads,⁵ and scanning probe tip electrodes^{6,7} have been successfully demonstrated. Although these approaches are able to produce laboratory test structures, they cannot be scaled up for the fabrication of circuits and systems containing organic devices because the processing techniques are highly specialized and time-consuming. Here we report the use of nTP⁸ to establish reliable electrical contact with

organic molecular layers. Pattern transfer is purely additive (so the organic molecules are not subjected to etchants, sacrificial resists, or developers and solvents), and multiple devices can be fabricated in parallel. Nanotransfer printing is fast, simple, and occurs readily at ambient conditions. Figure 1 illustrates the nTP process and the wide range of feature sizes—from nanometers to centimeters—accessible by this technique.

In this experiment, we chose conductive n⁺ (001) GaAs (Si-doped, 10¹⁸ cm⁻³) substrates rather than metallic bottom electrodes because well-established models that describe electrical transport across metal–semiconductor interfaces can be used to evaluate the nature of contacts formed by nTP and conventional evaporative methods.⁹ Gold (Au) and n⁺ GaAs form a Schottky diode contact with a barrier height of 0.7 V.¹⁰ The presence of a molecular layer between Au and n⁺ GaAs will modify the Schottky contact properties, manifested by changes in Au/GaAs junction electrical characteristics. Because the bottom electrode is a semiconductor, photoresponse experiments can be conducted in addition to the conventional current–voltage (*I*–*V*) measurements. The photoresponse results turned out to be the key to understanding how the top electrode fabrication method affects electrical transport.

Figure 1 shows the scheme of the nTP procedure for fabricating top Au electrodes for molecular junctions composed of 1,8-octanedithiol on n⁺ GaAs.¹¹ The n⁺ GaAs substrates are first stripped of their native oxide and then immediately exposed to saturated 1,8-octanedithiol vapor in a desiccator for 15 min. Control experiments involving different surface treatments¹¹ indicated that the majority of the 1,8-octanedithiol molecules chemisorb on the GaAs surface with a preferential orientation: only one end of the molecule reacts with the GaAs surface, yielding a molecular

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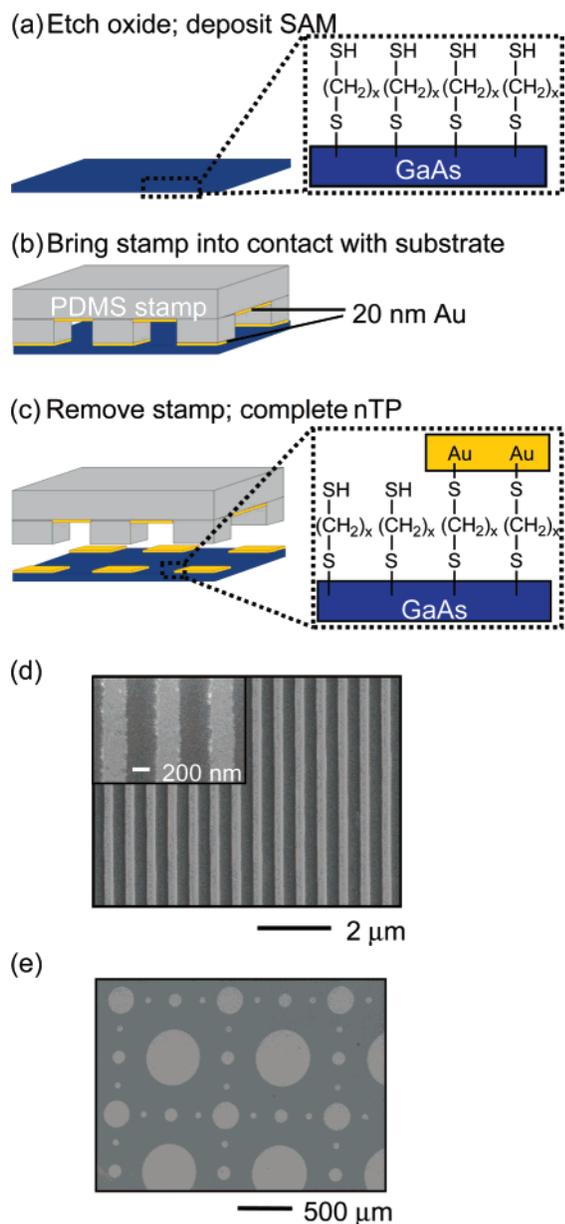


Figure 1. Schematic of the nanotransfer printing (nTP) procedure. (a) The GaAs substrate is first etched in concentrated NH_4OH or HCl for 2 min and then immediately exposed to 1,8-octanedithiol ($x = 8$) vapor for 15 min. (Solution deposition of the dithiol layer produced similar results.) (b) Gold-coated elastomeric PDMS stamp with appropriate relief features is brought into contact with the treated substrate. (c) Removal of the stamp from the substrate completes the printing process. Au on the raised part of the PDMS stamp is bonded and transferred to the dithiol-coated GaAs. Scanning electron micrographs of (d) 300-nm-wide Au lines printed on an octanedithiol-coated GaAs surface and (e) nTP Au/dithiol/ n^+ GaAs junctions used in the transport studies.

layer with unreacted thiol endgroups generally facing away from the substrate.¹² The idealized orientation of 1,8-octanedithiol on etched GaAs is depicted in the inset of Figure 1a. We also explored solution-immersion methods for depositing 1,8-octanedithiol on GaAs substrates;¹³ the conditions we used produced similar printing results. Prior to nTP, the treated GaAs substrates are rinsed thoroughly with ethanol to remove any multilayer buildup. A fresh gold-coated elastomeric poly(dimethylsiloxane) (PDMS) stamp

with chosen relief features is brought into contact with the treated GaAs substrate by hand; no additional pressure was applied to the stamp during this process. Removing the stamp from the GaAs substrate completes the pattern transfer process. The spontaneous formation of S–Au bonds^{14,15} at the treated GaAs/Au-coated stamp interface facilitates pattern transfer (Figure 1c). Because 1,8-octanedithiol chemically binds the Au patterns to the substrate, the patterns easily pass Scotch tape adhesion tests. In addition to anchoring the Au patterns permanently to the substrate, the 1,8-octanedithiol molecular layer also serves as the electrically active component in these molecular junctions. The capability of nTP in producing nanometer features is illustrated in Figure 1d, and its application to the fabrication of large-area devices is shown in Figure 1e.

To understand how the different contact fabrication methods can affect transport properties of molecular junctions, we compared the electrical characteristics of our nTP junctions with reference junctions whose top Au contacts were directly deposited. Control junctions were made by directly evaporating Au through a shadow mask (of the same design as the PDMS stamp so the resulting contact areas are the same) on freshly etched n^+ GaAs (i.e., no molecules between Au contacts and the GaAs substrate). Evaporated junctions were made by evaporating Au through a shadow mask onto 1,8-octanedithiol-treated n^+ GaAs wafers. Prior to Au evaporation, 1,8-octanedithiol is deposited on n^+ GaAs following the same procedure that is used to make nTP junctions. Care was taken to ensure that the molecular junction fabrication procedures up to the top electrode deposition were identical for nTP and the evaporated samples. In all cases, the Au films were deposited by electron beam evaporation at a rate of 10 \AA/s and have a thickness of 20–25 nm. The chamber pressure immediately prior to evaporation was $(2\text{--}5) \times 10^{-7}$ Torr. The samples (either PDMS or GaAs chips) were ~ 30 cm away from the source in a direct line-of-sight configuration. The samples were not cooled. Although there are more sophisticated approaches to the evaporation of top Au electrodes in order to minimize direct contact between the two electrodes,^{2(b),16} optimizing Au evaporation conditions is not the goal of this study. Rather, we aim to keep the experimental conditions, including GaAs oxide etching, dithiol deposition, and Au evaporation, constant for the three types of samples to achieve meaningful comparisons. Therefore, differences in the electrical characteristics of these devices reflect real differences in the nature of the contact that is attributable to the fabrication of top electrodes.

All transport measurements were performed in a standard probe station. The I – V measurements were made using an electrometer. Figure 2a shows four sets of I – V characteristics for nTP Au/1,8-octanedithiol/GaAs junctions with different contact areas (Figure 1e; dots with diameters of 62.5, 125, 250, and $500 \mu\text{m}$). The probe pressure was kept to a minimum¹⁷ to avoid damaging the Au electrodes or affecting the transport characteristics.¹⁸ We found that the current densities are independent of the contact area for the nTP devices. The scaling of total current with junction area

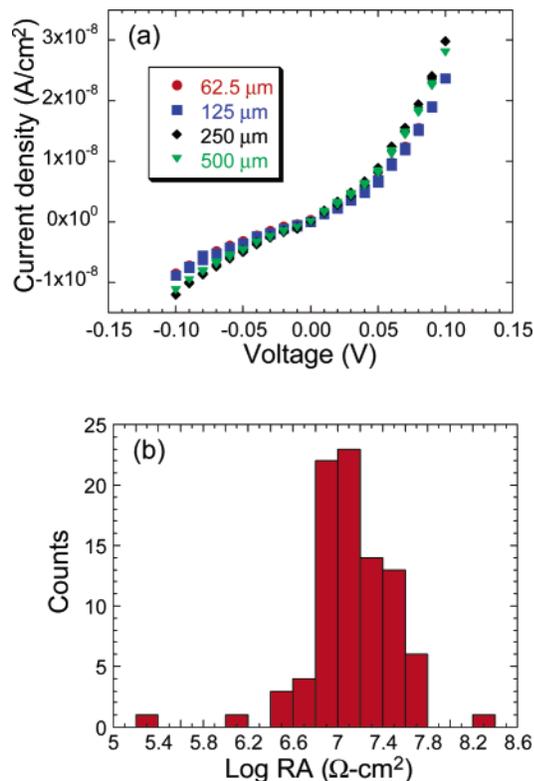


Figure 2. (a) Current density as a function of applied voltage. The measured current scales linearly with junction area. (b) Histogram revealing the reproducibility of the measured specific contact resistance (RA , R : resistance obtained from the linear region of the I - V curves between 0 and -0.1 V; A : area of the Au contact). RA is on a log scale. Devices (88) of various contact areas were measured; the RA of most devices is within a factor of 10 of each other.

indicates that current distribution is uniform in nTP junctions. In particular, transport is not dominated by edges. In the low-bias region (-0.1 to 0.1 V), the I - V characteristics are linear for negative bias and superlinear for positive bias. To evaluate electrical conduction through these junctions, we measured the resistance (R , the slope in the linear portion of the I - V curve) of 88 devices fabricated using 8 different batches of stamps and substrates as well as different 1,8-octanedithiol deposition methods (vapor versus solution deposition). The specific resistances (RA , where A is the junction area) for these devices are plotted in Figure 2b. Except for $\sim 2\%$ of the junctions, the measured RA values are within an order of magnitude of each other (between $3.5 \times 10^6 \Omega \text{ cm}^2$ and $4.6 \times 10^7 \Omega \text{ cm}^2$). When we examined the characteristics of molecular junctions in a given printed array, the spread is significantly less, and the RA values are within a factor of 2. Repeated measurements over the small-bias range shown here do not show changes in the diode characteristics. Nanotransfer printing is thus an effective method for fabricating electrical contacts to molecular layers in a reliable and reproducible fashion.

Figure 3 shows I - V characteristics for the control, evaporated, and nTP junctions (all with a $62.5\text{-}\mu\text{m}$ diameter). Although none of these diodes exhibits ideal Schottky diode behavior, it is still useful to analyze them within the thermionic emission model to obtain an *effective* barrier

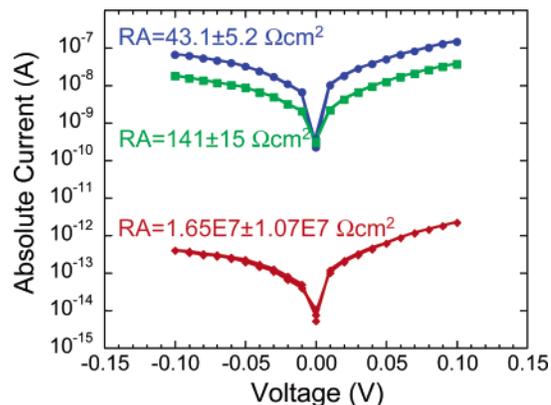


Figure 3. Absolute current levels (on a log scale) of two-terminal devices for applied voltage are between $+0.1$ and -0.1 V. The n^+ GaAs was maintained at ground, and the voltage was applied to the top Au contacts. All devices have the same area, $3 \times 10^{-5} \text{ cm}^2$. The mean and standard deviation values of RA for each type of sample are shown. For the control and evaporated samples, 10 I - V curves were used for the calculation. For the nTP samples, all except open and shorted curves were used. Control sample: Au contacts were fabricated by directly evaporating through a shadow mask onto a bare n^+ GaAs substrate (blue circles). Evaporated sample: direct evaporation of Au on a dithiol-treated n^+ GaAs substrate (green squares). nTP samples: contact printing of Au electrodes onto a dithiol-treated n^+ GaAs substrate (red diamonds).

height.¹⁰ The magnitude of the effective barrier height reflects the nature of transport through the contacts. For example, an effective barrier height lower than that expected from an ideal Schottky barrier height implies the presence of ohmic contacts, and a higher effective barrier height suggests tunneling through an insulator. The I - V characteristics of the control and evaporated samples are similar in shape and magnitude, and their extracted effective barrier heights are 0.55 and 0.58 V, respectively. These barrier heights are lower than the Schottky barrier height expected for Au on n^+ GaAs (0.7 V), indicating the presence of ohmic contacts in these junctions. Because the sample temperature rise during the short evaporation time (<20 s) is minimal, the ohmic contacts likely arise from the high dopant density of n^+ GaAs and the tendency of Au to alloy with GaAs.¹⁹ By comparing the RA from the I - V results to the specific contact resistance of a good ohmic contact on n^+ GaAs ($10^{-6} \Omega \text{ cm}^2$),²⁰ the fractions of contact areas with ohmic characteristics were determined to be 2×10^{-8} and 6×10^{-9} for control and evaporated junctions, respectively. Although these ohmic fractions are small, they are consistent with the measured current densities for the control and evaporated samples. Detailed analyses are published separately.²¹ These results suggest that, despite the presence of a molecular layer, ohmic Au/GaAs contacts also dominate electrical transport in the evaporated junctions.

The current levels for the junctions fabricated by nTP, however, are 5 orders of magnitude lower than the levels for both the control and evaporated samples. The extracted effective barrier height ranges from 0.82 to 0.91 V (0.87 V for the I - V trace shown in Figure 3) for junctions shown in Figure 2b. These values are significantly higher than those of the control and evaporated samples and are also higher

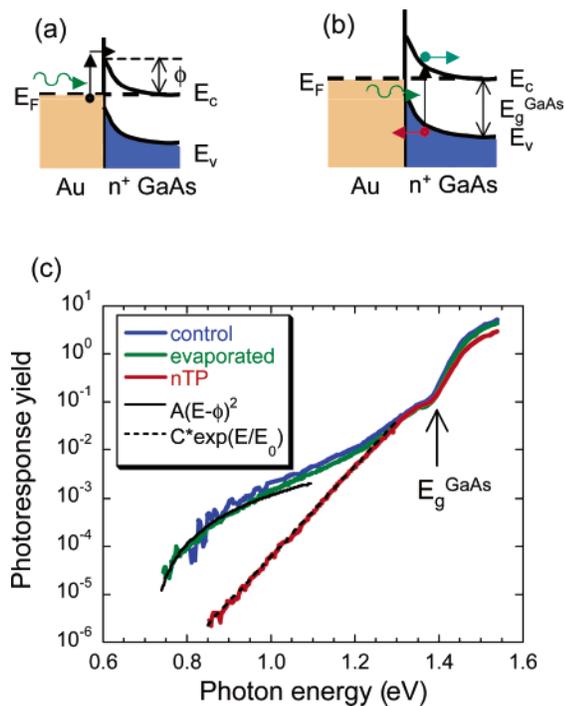


Figure 4. (a) Schematic of dominant photocurrent process when a below- E_g^{GaAs} photon is absorbed in the Au/n⁺ GaAs junction. (b) Schematic of dominant photocurrent process when an above- E_g^{GaAs} photon is absorbed in the Au/n⁺ GaAs junction. (c) Photoresponse yield (on a log scale) as a function of photon energy from 0.7 to 1.55 eV for control (blue), evaporated (green), and nTP junctions (red). All junction areas are 2×10^{-3} cm². The solid black lines are fits to $A(E - \phi)^2$, where A is a constant. The dotted black line is a fit to $C \exp(E/E_0)$.

than that expected for Au/n⁺ GaAs Schottky contact. The estimated ohmic fraction in the nTP junctions is $\sim 7 \times 10^{-14}$; this corresponds to an ohmic contact size of ~ 0.01 nm² for our largest dots (area = 2×10^{-3} cm²). Because such a value is smaller than atomic cross sections, we thus conclude that Au/n⁺ GaAs ohmic contacts are not present in the nTP junctions. The fact that the effective barrier height in the nTP junctions is higher than that for Au/n⁺ GaAs Schottky contact signifies a different transport mechanism, such as tunneling through an insulating barrier, in these nTP devices.

To characterize electrical transport in these junctions further, we measured the energy dependence of the photocurrent at zero bias²² (i.e., the current that is produced between Au and n⁺ GaAs by photon absorption). Figure 4c shows the photoresponse of the control, evaporated, and nTP samples as a function of photon energy (E) from 0.7 to 1.55 eV. Below the GaAs band-gap energy ($E_g^{\text{GaAs}} = 1.4$ eV), electrons in the Au electrode absorb photon energy to overcome the barrier presented by the GaAs (Figure 4a). This process is known as internal photoemission (IPE), and it is analogous to the photoinduced emission of electrons from a metal to vacuum. The IPE experiment is a well-established method for measuring Schottky barrier heights in inorganic materials:¹⁰

$$Y \propto (E - \Phi_{\text{IPE}})^2$$

Y is the photoresponse yield (photocurrent normalized by photon flux), E is the photon energy, and Φ_{IPE} is the barrier height determined from IPE. Here, we have applied this method for determining barrier heights in our junctions. For $E < E_g^{\text{GaAs}}$, both the control and evaporated samples show classic Schottky behavior (solid black line in Figure 4c; E^2 dependence). Schottky barrier heights extracted from the IPE data for both samples (~ 0.7 V) are consistent with the Schottky barrier height for Au/n⁺ GaAs. From the ratio of IPE yield coefficients for evaporated and control samples, we estimate that $\sim 35\%$ of the contacts in the evaporated sample comprise direct Au/GaAs contacts. The fact that IPE barrier heights are larger than those extracted from the $I-V$ curves confirms the presence of ohmic contacts, through which current flows predominantly under bias although they do not contribute to the photocurrent. However, the nTP junction exhibits an exponential E dependence over 3.5 decades (dashed black lines in Figure 4c), indicating that the photoexcitation process involves disordered materials.²³ Attempts to extract a barrier height from the nTP sample IPE data using an E^2 dependence produced a value greater than 1 V. Such a value is nonphysical for Au/GaAs contacts and implies the absence of a direct Au/GaAs Schottky contact in the nTP junctions.

Although the reduced current levels in the nTP junctions (Figure 3) could be attributed to poor electrical contact between the printed top Au electrode and the molecular layer (e.g., the presence of air gaps, thereby resulting in a smaller effective contact area), the IPE results (Figure 4c) rule out this possibility. If a smaller effective contact area were responsible for the reduced current levels in the nTP junctions, we would expect the photoresponse spectra acquired on the nTP junctions to display the same E^2 dependence as those observed in the control and evaporated junctions but with 10^5 times smaller photocurrent signals. This is not seen experimentally. Consistent with the $I-V$ results, the IPE data also point to a different transport mechanism in the nTP junctions, namely, electrical conduction between Au and GaAs must occur through the 1,8-octanedithiol layer.

Additional information on transport through the molecular layer can be obtained from the above-band-gap photoresponse results. Above E_g^{GaAs} , photon absorption in the GaAs depletion region produces electron-hole pairs that can separate and migrate to the electrodes (Figure 4b; holes to Au and electrons to n⁺ GaAs, respectively). We found that the photoresponse yield above E_g^{GaAs} for the nTP junction is merely a factor of 2 smaller than those of the control and evaporated samples (Figure 4c). This observation further confirms good electrical contacts between Au and GaAs and argues against smaller effective contact areas in the nTP junctions. Because the photogenerated electrons can move readily into the GaAs bulk (Figure 4b), the transport of photogenerated holes to Au is the limiting step in the above-band-gap photocurrent process. In the nTP junctions, the holes must traverse the dithiol molecular layer to reach the Au electrode because direct Au/GaAs contacts are absent. The high photoresponse yield in the nTP junctions when E

$> E_g^{\text{GaAs}}$ thus indicates that hole transport is efficient in the octanedithiol layer, consistent with recent work from other groups.²⁴

We showed that the electrical transport mechanism in molecular junctions depends critically on the contact fabrication method. Similar electrical behavior in the control and evaporated junctions indicates that evaporating Au on 1,8-octanedithiol leads to direct contacts between Au and GaAs. The presence of such contacts dominates the I - V characteristics of evaporated molecular junctions and thoroughly masks transport through the molecular layer. On the contrary, direct Au/GaAs contacts are not found in the nTP junctions. Electrical transport in these nTP junctions occurs through the 1,8-octanedithiol molecular layer, which has a much lower conductivity than direct Au/GaAs contacts. In addition, we found hole transport through the 1,8-octanedithiol molecular layer to be efficient. Hence, nTP is a promising new way of making electrical contacts in molecular devices with reproducible characteristics.

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