

All-Dry Deterministic Transfer of Thin Gold Nanowires for Electrical Connectivity

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Metallic nanowires (NWs) exhibit a number of interesting properties, such as high conductivity, flexibility, and cold-weldability, making them ideal for nanocircuits. They are usually adsorbed on substrates by depositing a colloidal solution of NWs on the surface. However, they remain randomly scattered and solvent residues may contaminate/ degrade the sample. This study presents a method for forming electrical contacts with gold nanowires based on all-dry deterministic transfer. The process begins with the adsorption of gold nanowires by drop casting the colloidal solution onto a viscoelastic substrate. These wires are transferred to selected locations on the substrate, minimizing manipulation with fabrication times a factor of 2 shorter than direct drop casting deposition, preserving surface and sample conditions, and improving the fabrication of nanocircuits. Atomic force microscopy is used to manipulate the NWs for the final connections, which have contact resistances of a few ohms. To illustrate the technique, three different examples of applicability are presented. This work is expected to be a starting point for expanding the potential of deterministic transfer that is successfully used in 2D materials. For example, to study local electrical transport in heterogeneous samples such as van der Waals heterostructures and twisted layers of 2D materials.

Yang Lu et al. published a seminal article entitled “Cold welding of ultrathin gold nanowires”,^[11] in which they used transmission electron microscopy to demonstrate crystalline cold welding of ultrathin (3–10 nm in diameter) gold NWs upon mechanical contact. The authors concluded that this process, combined with other nanofabrication techniques, has the potential to be used for bottom-up assembly of metallic 1D nanostructures and next-generation interconnects for extremely dense logic circuits. Building on this work, we have demonstrated the feasibility of constructing highly conductive and reconfigurable metallic nanoelectrodes using a novel technique called SPANC (Scanning Probe-Assisted Nanowire Circuitry), which involves the manipulation and cold welding of gold nanowires using atomic force microscopy (AFM).^[12]

In parallel, at the turn of the century, the field of 2D materials also emerged and revolutionized materials

science and related disciplines.^[13,14] These materials require specialized fabrication techniques, in particular the deterministic transfer of 2D crystals to specific locations,^[15] which is crucial for exploring the unique properties of their assemblies, also known as van der Waals heterostructures. For example, the combination of 2D materials with high precision positioning opens up new opportunities to address challenges in fundamental physics and applications.^[16] Initially, transfer

1. Introduction

The blossoming of metallic nanowire (NW) technology since the turn of the century has enabled a number of applications ranging from flexible transparent conductive films,^[1–3] touch sensors,^[4,5] conductive polymer nanocomposites,^[6] photovoltaic cells,^[7,8] or thermal energy storage,^[9] among others. Several metals have been used for NW synthesis with silver, copper, and gold being the most commonly used elements.^[1,2,6,10] In 2010

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methods used sacrificial polymer layers and required a wet process at some point.^[15] To overcome the issues associated with these methods, all-dry transfer procedures using viscoelastic stamps were developed.^[17] This technique has evolved into various applications such as the precise positioning of 2D materials on thermal strain microactuators,^[18] manipulation of individual nanowires,^[19] or controlled nanopositioning of individual nanoparticles on photonic nanostructures,^[20] among others.

In this work, we introduce a new methodology for fabricating nanoelectrodes for device characterization and circuit repair that takes advantage of the best features of SPANC and all-dry deterministic transfer. In SPANC we deposited nanowires directly onto a substrate by drop casting. Now, we add another step consisting of first drop casting the nanowires onto a stamp that allows deterministic transfer of the nanowires onto a substrate for subsequent nanomanipulation with an AFM tip for electrical interconnection of different nano-objects. We demonstrate the effectiveness of our approach with three examples: a four-terminal few-layer graphene device, the repair of a gold nanoelectrode, and the electrical characterization of a few-layer MoS₂ device under different illumination conditions.

The major advantages of this approach are the high precision of the final position of the nanoelectrodes and the optimization of the handling time on the sample. In addition, our method minimizes contamination and fabrication risks because it does not require any pre-treatment or exposure of the sample to liquids or gases. A clear advantage of dry transfer over previous methods based on drop casting is its application to liquid-sensitive nanomaterials, such as organic semiconductors, where one could not drop cast nanowires dispersed in organic solvents. All this results in a non-invasive and very sample-friendly fabrication method.

2. Results and Discussion

Our new method is inspired by previous work on the deterministic transfer of soft-electrodes using poly(dimethylsiloxane) (PDMS)^[21] and in our experience with gold nanowires adsorbed on surfaces.^[12] We use a fresh piece of a transparent PDMS-based viscoelastic polymer (Gel-film from Gel-Pak) as a stamp (**Figure 1a**), which is cleaned by a short oxygen plasma treatment (**Figure 1b**; see Experimental section for details).

We start by preparing a colloidal suspension of gold NWs (see Experimental section). We then deposit a random distribu-

tion of gold nanowires on the so treated stamp by drop casting the suspension (**Figure 1c**). After this, we treat the stamp again with another short oxygen plasma cycle (**Figure 1d**). This second treatment removes the residues of organic compounds characteristic of nanowire suspensions and, importantly, cleans the surface of the nanowires of the capping molecules (surfactant) used for colloidal stability.^[22] In addition, the plasma treatments make the stamp surface hydrophilic, which favors the retention of most of the remaining surfactant on the stamp during the transfer step.^[23] This ensures a clean substrate without capping molecules. We then inspect the stamp surface using optical microscopy (see Supporting Information Figure S1) and select appropriate sets of gold nanowires, which we deterministically transfer to the substrate (**Figure 1e**). As the stamp is transparent, it is possible a simultaneous visualization of the target substrate and the nanowires on the stamp just using an optical microscope. We then position the nanowires using a XYZ micromanipulator where the stamp is placed. Finally, we use an AFM tip to nanomanipulate the gold nanowires on the surface, and assemble nanoelectrodes by cold welding (**Figure 1f**), as described in detail in Moreno-Moreno et al.^[12] For example, in that work it is discussed that the optimal geometry for cold welding is head-to-side with a minimum force of the order of 100 nN. The transfer process can be repeated as many times as needed with minimal sample disturbance.

We emphasize that AFM can also manipulate gold nanowires on both untreated and oxygen plasma treated stamps using the same procedure described for nanowires adsorbed on a conventional substrate. **Figure 2a** shows three nanowires adsorbed on the stamp by drop casting. **Figure 2b** shows the same three nanowires after AFM manipulation. Finally, **Figure 2c** shows the whole assembled set successfully transferred to a SiO₂/Si substrate. This approach guarantees minimal further manipulation of the NWs in the desired configuration and presents two main advantages. First, because we assemble the circuit on a viscoelastic stamp and then transfer it to a sample substrate, it reduces the time spent working on the substrate, which is critical for samples that degrade in ambient conditions. Second, it minimizes potential problems during sample manipulation.

We tested the feasibility of this new method in several ways. **Figure 3** shows the fabrication of a graphene four-terminal device for electrical resistance characterization. This architecture is similar to the two-terminal scheme, but it allows the resistance of a nano-object to be measured experimentally without contact resistances. When the contact resistance is greater than the intrinsic resistance of the nano-object, as in the case of few-layer graphene, this configuration becomes mandatory. We start by transferring a few-layer graphene flake obtained by micromechanical exfoliation to a SiO₂/Si substrate with six prefabricated microelectrodes by shadow mask assisted thermal evaporation (see Supporting Information Figures S2 and S3). The NWs are then transferred and manipulated on the substrate surface, as described above, resulting in a clean (**Figure 3a**) and functional device with an electrical resistance of 33 Ω (**Figure 3b**), a reasonable value for this type of circuit.^[12]

We further tested the ability of this method to repair microstructures. To this end, we use a circuit fabricated by electron beam lithography (e-beam) on a SiO₂/Si substrate (**Figure 4**). Note that e-beam is a demanding lithography technique that

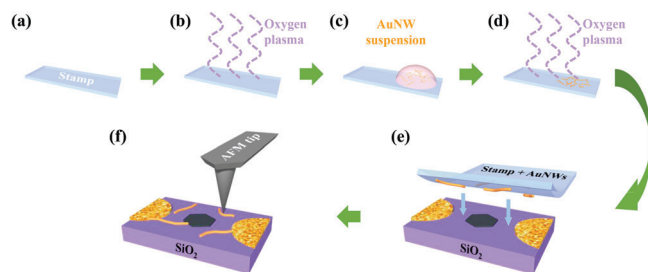


Figure 1. Scheme of the experimental procedure. a) Fresh piece of viscoelastic stamp. b) First oxygen plasma (10 s). c) Gold NWs deposited on the viscoelastic stamp by drop casting. d) Second oxygen plasma (10 s). e) Deterministic transfer of NWs. f) Assembly of nanoelectrodes by AFM manipulation.

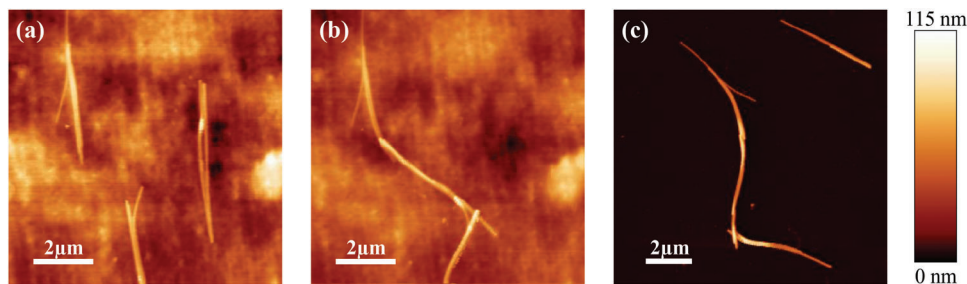


Figure 2. Topographic images of: a) Gold NWs deposited on a piece of PDMS, b) Nanoelectrode formed by in situ AFM manipulation of the nanowires shown in a), and c) Nanoelectrode in b) after deterministic transfer to a SiO₂/Si substrate.

allows the fabrication of delicate micro- and nanocircuits that may require a significant investment of time and resources. Therefore, it is important to provide a suitable technique for repairing these circuits. The device shown in Figure 4a presents a narrow central electrode (a constriction $\approx 10 \mu\text{m}$ long and 600 nm wide) that contains two narrower auxiliary microelectrodes at either end of this constriction to measure the voltage drop across it. The configuration of the electrodes allows us to measure the electrical resistance of this constriction. Electrostatic discharge is a common factor that leads to failure of nanocircuits, as in the case of the thin right electrodes shown in Figure 4b,c. Because of the small size of the gap and the short distance between its edges, we decided that it would be a good test sample for our method. Again, the deterministic transfer allows us to have good control over the final position of the NWs, as only a low number of nanomanipulations are needed to contact the electrode side with the nanowire end. Figure 4d,e show the two-terminal current-voltage characteristics of both repaired electrodes. Here we see good metallic behavior with electrical resistances of 200 and 175 Ω , respectively. These values are quite close to the electrical resistance of the constriction, which has a value of 167 Ω . Such good electrical resistances are due to the material that both structures are made of and the clean surfaces of the substrate and the gold structures.

In the last example, we investigate the performance of a two-terminal mechanically exfoliated MoS₂ few-layer device (Figure 5a) under different illumination conditions. First, we prefabricate four gold microelectrodes by shadow mask-assisted thermal evaporation, selecting electrode #1 for electrical contact.

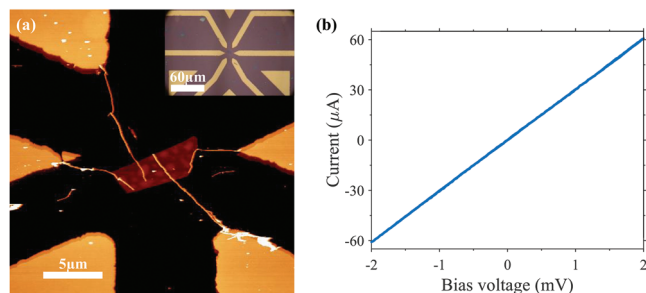


Figure 3. a) Topographic AFM image of a few-layer graphene flake connected by four gold nanoelectrodes. Inset: wide field of view optical image of this device. b) Current versus voltage characteristics of the graphene device in (a), showing ohmic behavior.

Second, we assemble electrode #2 by transferring and manipulating several gold NWs before cold welding them in place. Finally, we transfer the MoS₂ flake onto electrodes #1 and #2. Therefore, in the resulting electrical circuit, the gold nanoelectrode is encapsulated between the insulating SiO₂ substrate and the flake.

Figure 5b shows the current versus voltage characteristics obtained by illuminating the sample with an incandescent lamp at a temperature of 3000 K, compared to the results obtained under dark conditions. The excess in current is due to the photocurrent generated by the photoelectric effect.^[24] It is noteworthy that the current increases by about three orders of magnitude when the device is illuminated.

3. Conclusion

We have presented a new method for electrical interconnection of gold nanowires based on deterministic transfer from a viscoelastic stamp. This process allows for a significant reduction in processing time (up to a factor of two compared to the direct drop casting process) while maintaining a clean and contamination-free substrate. We have demonstrated the capabilities of this methodology for fabricating devices for 2D materials characterization and microcircuit repair, achieving contact resistances of a few ohms. We have also demonstrated nanomanipulation of gold nanoelectrodes on the viscoelastic stamp, allowing deterministic transfer of the entire nanoelectrode at once. This is noteworthy because it dramatically minimizes the work time on the substrate. Future research will explore the potential applications and limitations of this method in various fields. We anticipate that the ability to assemble nanoelectrodes ex situ has the potential to be beneficial for the study of environmentally sensitive nanomaterials, as well as its reconfigurable nature for the study of electrical transport in heterogeneous samples such as van der Waals heterostructures and twisted layers of 2D materials.

4. Experimental Section

Optical Microscopy: A Zeiss Axiovert microscope equipped with 5 \times , 10 \times , 20 \times , 50 \times , and 100 \times objectives was used. Both bright- and dark-field images were taken to identify the suitable nanowires (see Supporting Information). Optical microscopy was also used to monitor the deterministic transfer process.

Atomic Force Microscopy: AFM measurements were carried out using a Nanotec Electronica SL based AFM. WSxM software was employed for data acquisition and image processing.^[25,26] All the topographic images

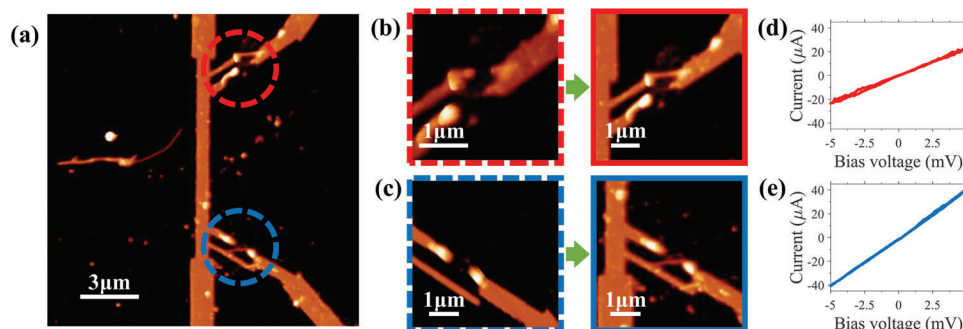


Figure 4. a) Topographic AFM image of a gold electrode constriction with two auxiliary electrodes repaired with gold NWs after current overload. b) Magnification of (a) of the upper lateral electrode before (left) and after (right) repair with a gold NW. c) Same as in (b) for the lower lateral electrode. In this case, two nanowires were used to repair this electrode. d and e) Current versus voltage characteristics of the repaired upper and lower lateral electrodes, respectively.

shown in this work were acquired in dynamic mode. Both the topographic images and the gold NW electrode-assembly were performed using silicon tips with a nominal spring constant of 3 N m^{-1} (Nanosensors PPP-FM). Conductive diamond coated tips were used with a nominal spring constant of 6.5 N m^{-1} (Budget Sensors All-In-One-DD) to check the electrical connections of the circuits.

Thermal Evaporation and Evaporation Masks: First, 7–10 nm of chromium followed by $\approx 60 \text{ nm}$ of gold was deposited on SiO_2/Si substrates (300 nm oxide silicon grown thermally on a Si(111) crystal). Nickel stencil masks were used to define the electrode geometry on the substrates (see Supporting Information).

Colloidal Suspension of Nanowires: A suspension of synthesized gold nanowires was prepared by following a modification of the literature method described in.^[12] This method was based on the well-established three step protocol for nanorods synthesis published by Murphy et al.^[27] In this synthesis process, gold seed nanoparticles were obtained from the reduction of HAuCl_4 solution by NaBH_4 in the presence of sodium citrate. The seed particles grow into nanowires when added to a growth solution containing a mixture of HAuCl_4 (Au^{3+}). Further details of the synthesis were described in Moreno-Moreno et al.^[12] The final aqueous suspension contains not only gold nanowires, but also by-products of other gold structures as well as residues of agents used in the process, such as hexadecyltrimethylammonium bromide (CTAB), which was used as surfactant.

Deposition of Nanowires: First, the colloid was heated to 30°C to dissolve crystallized CTAB structures that were usually present in the suspension. To resuspend aggregated nanowires, the suspension was placed in a vortex mixer for 15 s, and then sonicated it in an ultrasonic bath (30°C , 37 kHz, and 380 W) for 5 min. After that, an $8 \mu\text{L}$ drop was casted onto the cleaned PDMS and allowed it to incubate for 45 s. Then, the PDMS surface

was rinsed with deionized water at the same temperature. Finally, it was dried with a flow of N_2 gas. Particular attention was paid to carry out this process gently, keeping the suspension at $\approx 30^\circ\text{C}$ to avoid the formation of CTAB crystals.

Stamp Preparation: A fresh piece of a transparent PDMS-based viscoelastic polymer (Gel-film from Gel-Pak) was used as a stamp. Before and after nanowire deposition, the stamps were cleaned by short oxygen plasma cycles (Diener electronic Femto plasma system using a 40 kHz RF power supply). The plasma power was 35 W and the exposure time was 10 s, with a pressure of 0.18–0.20 mbar, and an oxygen flow rate of 1.5 sccm. This treatment removes hydrocarbon groups from the stamp surface,^[28] reducing the contamination during the transfer step. It also oxidizes the viscoelastic polymer, producing silanol terminations on its surface and a thin silica layer,^[29] leaving the surface hydrophilic^[30–32] and ensuring a more uniform coverage when depositing a water droplet suspension with nanowires. Longer plasma sessions induce surface cracks, resulting in unwanted hardening of the surface mask.

Nanomanipulation of Nanowires: Nanomanipulation of the nanowires was performed using the lithography option of WSxM.^[12,25] This option allows to switch between dynamic and contact mode, which was used to manipulate the NWs according to predefined patterns. Normal forces ranging from 90 to 170 nN were applied.

Electrical Measurements: Once the devices were prepared, a Keithley Series 2400 Source-Meter unit was used to obtain the current versus voltage characteristics shown in this work.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

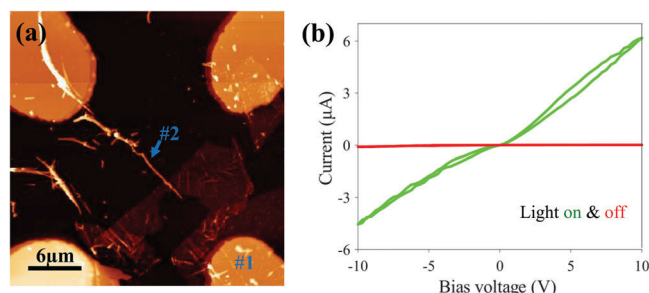


Figure 5. a) Topographic AFM image of a MoS_2 flake electrically connected by a prefabricated gold microelectrode (#1) and a gold NW nanoelectrode (#2). b) Current versus voltage characteristics obtained by illuminating the sample with an incandescent lamp (green curves) and under dark conditions (red curves).

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

atomic force microscopy, deterministic transfer, nanocircuits, nanoelectrodes, nanowires

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