

Directed Integration of Tetracyanoquinodimethane-Cu Organic Nanowires into Prefabricated Device Architectures**

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1D nanostructures (such as nanotubes and nanowires) of semiconductor materials have attracted a lot of interest in recent years due to their potential applications in optical and electronic nanodevices such as chemical and biological sensors.^[1–6] However, the bottleneck to making functional nanodevices has been the difficulties involved in connecting these nanostructures to microscale electrodes. Many methods for fabricating nanowire-based devices have been explored,^[7–10] but most of these techniques require complex post-processing. For example, the “pick-and-place” approach has been successful for making individual devices, such as field-effect transistors and chemical sensors,^[11,12] however, it cannot be used for the reproducible, large-scale fabrication of dense, low-cost device arrays. Processes directly integrating growth into device fabrication, such as the precise and rational growth of nanowires within prefabricated device architectures, are highly desirable since they will markedly simplify the overall device assembly while avoiding the deterioration of the nanowires during processing. The lateral bridging growth of nanostructures was first demonstrated for GaAs nanowhiskers grown by metal–organic vapor phase epitaxy (MOVPE) from vertical ridges on a GaAs substrate.^[13] Recently, Williams and co-workers and Yang and co-workers have successfully grown Si nanowires across a trench on a Si substrate.^[14–16] The lateral growth of ZnO nanowires across a Si trench via a vapor–solid (VS) method has also been reported.^[17] All these examples demonstrate that nanowire growth and device fabrication can be achieved simultaneously and suggest that lateral bridging growth techniques may be a viable technology for the reliable integration of nanowires into dense arrays for sensors and other devices.

The charge-transfer organic compound tetracyanoquinodimethane-Cu (TCNQ-Cu) has attracted much attention because of its intriguing structural, electronic, and optical properties, and its potential applications in electrical and optical memory devices, sensors, and magnetic devices.^[18–20] Bulk and thin-film TCNQ-Cu devices have been widely studied in the past.^[21,22] While the properties of TCNQ-Cu organic nanowires offer many advantages over their bulk and thin-film counterparts, their integration into high-density memory and sensor arrays is limited by the sensitivity of this organic nanomaterial during normal nanofabrication processing steps. TCNQ-Cu nanowires are sensitive to electron-beam irradiation, ruling out electron-beam lithography and focused ion-beam deposition as processing techniques for their integration into devices. Such materials are also too soft to be processed by methods such as sputtering, etching, or milling. Therefore, direct nanowire growth between prefabricated electrodes appears to be the most promising method for the fabrication of single-crystal organic nanowire devices.

In this paper, we report a facile, low-temperature technique for the synthesis of single-crystal TCNQ-Cu organic nanowires between prefabricated electrodes by reactive chemical vapor deposition,^[23,24] demonstrating the self-assembled integration of organic nanowires into devices. Compared to current synthesis processes for inorganic nanowires and carbon nanotubes, this method avoids the high temperatures that often damage pre-existing electrodes and other microelectronic components. The lateral bridging growth method used here is demonstrated to be a reproducible method for the directed assembly and integration of TCNQ-Cu nanobridges into prespecified locations on different substrates, eliminating the need for subsequent assembly processes. We are able to effectively synthesize high-aspect-ratio and dendrite-free single-crystal TCNQ-Cu semiconducting nanowires with controlled dimensions. Electrical measurements show that the nanowires are in good contact with the prefabricated electrodes and possess electrical-switching properties.

The TCNQ-Cu nanowires are grown by the reaction of TCNQ vapor with Cu via a selective VS reaction mechanism according to Equation 1.^[23,24]

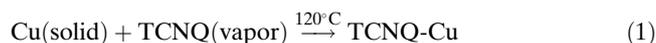


Figure 1 shows a dense forest of TCNQ-Cu nanowires held perpendicular to the thin planar Cu film from which they are grown and in good mechanical contact with the film. At the

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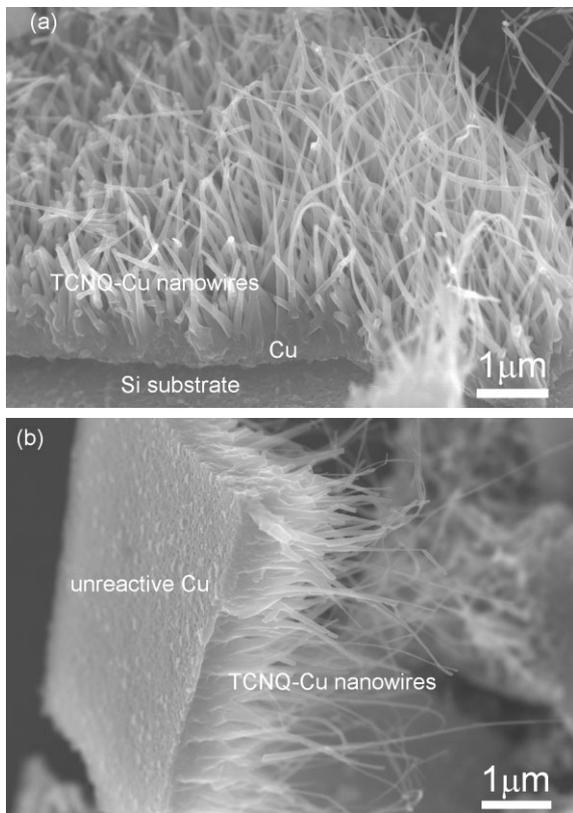


Figure 1. Scanning electron microscopy (SEM) images of TCNQ-Cu nanowires grown on a Cu (50 nm)/Si substrate at 120 °C.

120–130 °C temperatures utilized here for TCNQ-Cu nanowire growth, the Ti/Au electrode materials are inert, and are not consumed or damaged. Thus, 70 nm Ti/Au electrodes are first deposited onto the Si substrate, followed by a 50 nm thick Cu layer. In order to laterally limit the growth of TCNQ-Cu nanowires to the sides of the electrodes, an additional 100 nm thick Au layer is deposited to prevent the TCNQ vapor from reacting with the upper surface of the Cu layer. The top Au layer also serves as a top electrode for making good contact with the nanowires. After the photolithography and electron-beam lithography steps, Cu is only exposed at the middle of the sidewalls of the trench between the Ti/Au electrodes, as shown schematically in Figure 2a. The TCNQ-Cu organic nanowires grow laterally from the exposed Cu surface between the Au and Ti/Au electrode layers (Fig. 2b). These nanowires are thus grown on substrates with prepatterned electrodes when exposed to TCNQ vapor inside a 2 in. quartz tube furnace at 120–

130 °C for approximately 1–2 h under a 50 sccm flow of Ar (high purity, 99.998 %).

The TCNQ-Cu nanowires are found to selectively grow from the exposed Cu regions and grow laterally between the electrodes perpendicular to the exposed Cu layer. During the growth process, some nanowires span the gap and are welded with the Cu sidewalls on the opposite side, forming solid connections (Fig. 2c). Single-crystal semiconducting TCNQ-Cu nanowires can be produced by this VS reaction technique, and this growth process will be the subject of a separate report. The TCNQ-Cu nanowires are typically 20–50 nm in diameter and can span gaps of up to several micrometers (Fig. 3). The density of nanowires between the electrodes can be controlled by the thickness of the Cu layer, the growth temperature, and the growth time (Fig. 2c and d). When the growth temperature is 120 °C and the Cu thickness is less than 50 nm, only one nanowire can be grown between the electrodes. At a growth temperature of 130 °C, higher densities of nanowires can be grown between the two electrodes, allowing a larger surface area of TCNQ-Cu to be exposed to the ambient, and thereby creating the potential for high sensitivity. By virtue of the self-assembled connection between the two electrodes, the nanowires are automatically integrated into an electrically accessible device structure, which is quite attractive for sensors and other device applications requiring electrical conduction.

Micro-Raman spectroscopy investigations have been performed in order to characterize the self-assembled nanowires between the electrodes. Figure 4 shows the Raman spectrum

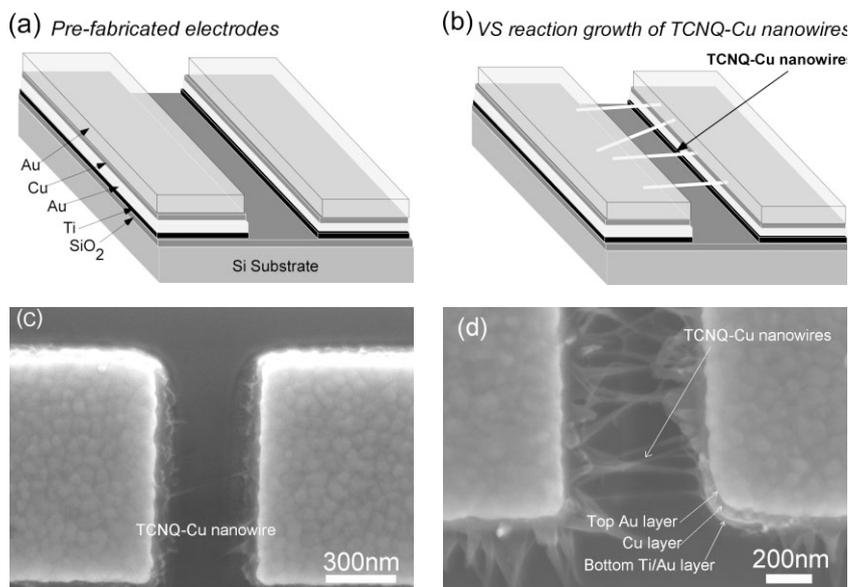


Figure 2. Cross-sectional schematic illustrating various steps in the growth of TCNQ-Cu nanowire bridges between prefabricated multilayer electrodes. a) Multilayered metal microstructure obtained by photolithography and electron-beam lithography patterning on a SiO₂/Si substrate. b) Schematic of nanowires grown directly between the prefabricated electrodes. SEM image of c) a single TCNQ-Cu nanowire and d) several nanowires grown between prefabricated multilayered metal electrodes.

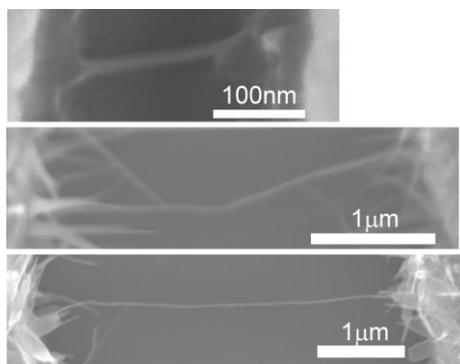


Figure 3. SEM images of single TCNQ-Cu nanowires with ca. 20 nm diameters spanning 200 nm, 3 μm , and 4 μm electrode gaps.

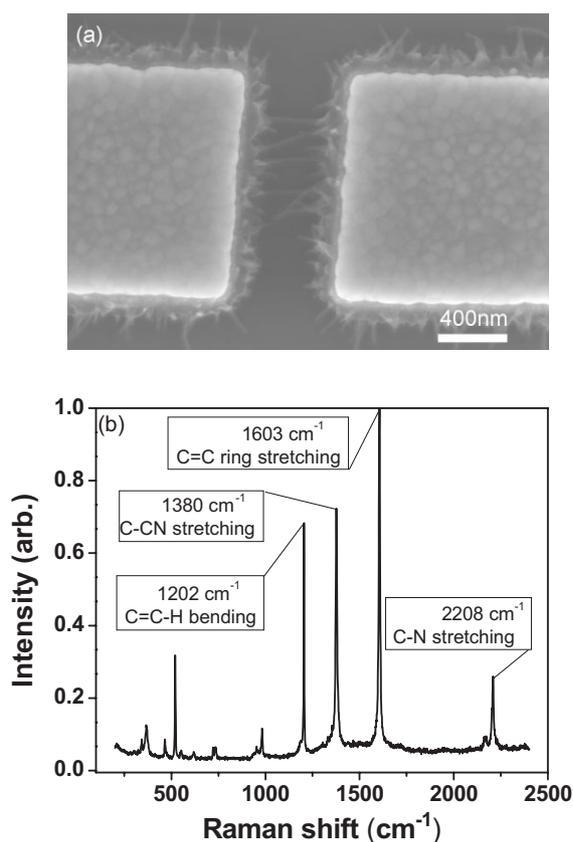


Figure 4. a) SEM image of TCNQ-Cu organic nanowires grown between prepatterned electrodes. b) Micro-Raman spectrum of the as-grown TCNQ-Cu nanowires shown in (a).

of nanowires grown between the electrodes, confirming that they are indeed composed of TCNQ-Cu with characteristic principal vibration modes at 1202 cm^{-1} (C=CH bending), 1380 cm^{-1} (C-CN wing stretch), 1603 cm^{-1} (C=C ring stretching), and 2208 cm^{-1} (C-N stretch). Compared with the Raman spectrum of a neutral TCNQ film, the C-CN stretching mode of TCNQ-Cu shifts from 1445 cm^{-1} to 1380 cm^{-1} , due to complete charge transfer between Cu and TCNQ.^[25]

To confirm the integrity of the nanowires and to characterize their electrical properties, current-voltage (I - V) measurements have been obtained for the electrodes before and after the growth of TCNQ-Cu nanowires, as shown in Figure 5. Prior to the growth of nanowires, no current is measured between the electrodes, indicating that current transport occurs exclusively through the nanowire bridges. After nanowire growth, the symmetric character of the I - V curve, along with the large current values measured for devices incorporating several TCNQ-Cu nanowires between the electrodes, indicates that the nanowires make a good electrical connection to both the electrodes.

This technique shows great promise for reproducible device fabrication. In this preliminary study, nanowires are found to bridge over 80 % of 50 prefabricated electrode pairs. In addition, 90 % of the devices exhibit symmetric I - V curves. Moreover, the electrical properties of the as-synthesized nanowire devices are seen to be stable in air.

Organic compounds are promising candidates for memory devices because of their diversity of compositions and structures, ease of fabrication, low cost, and fast response.^[26,27] TCNQ-Cu is a widely studied semiconductor with potential applications in optical and electrical switching devices. The resistivity of this material switches from a high-impedance state to a low-impedance state within a few nanoseconds upon the application of an electric field or under optical excitation.^[18,19] Figure 6 shows typical I - V curves obtained for a TCNQ-Cu nanowire and for multiple nanowires grown between a $0.5\text{ }\mu\text{m}$ wide electrode trench structure upon cyclically sweeping the voltage up and down. These measurements

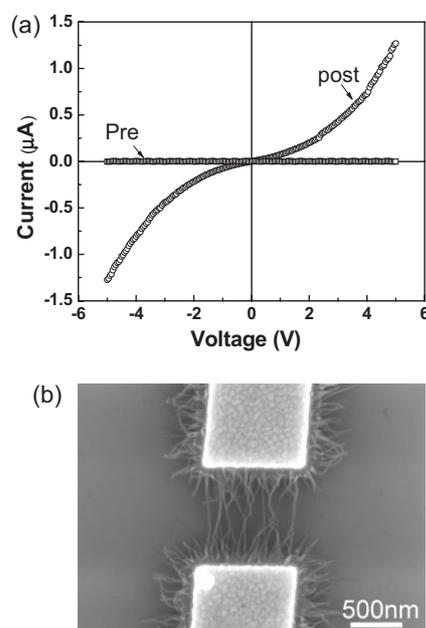


Figure 5. a) Current versus voltage curves measured between the electrodes before and after the growth of TCNQ-Cu nanowires (only scanning voltage at "ON" state). b) SEM image of the TCNQ-Cu nanowire bridging electrode structure.

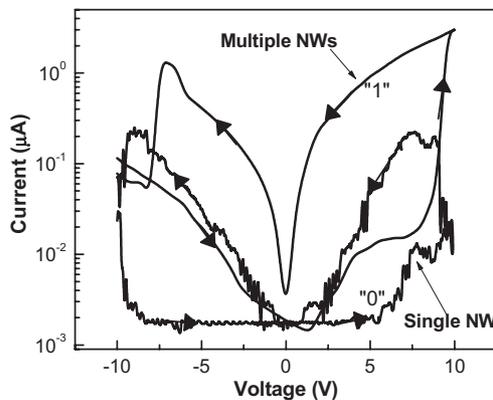


Figure 6. Typical room-temperature I - V characteristics of a single TCNQ-Cu organic nanowire and multiple nanowires bridging between electrodes indicating a reversible bistable switching behavior. The arrows show the voltage sweep directions.

have been made in air. The I - V curves exhibit reversible hysteretic switching and memory behavior. As the voltage bias is increased from 0 to +10 V, the current increases monotonically at low biases until a sudden jump in current is observed at a positive threshold voltage (V_T) of approximately +7 V. The TCNQ-Cu nanowire remains in the high-current state as the voltage bias is increased to +10 V and while the voltage is lowered from +10 to 0 V. In contrast, the TCNQ-Cu nanowire remains in the low-current state if the bias is not allowed to exceed this threshold voltage. Likewise, once the TCNQ-Cu nanowire is switched to the high-current state ("1"), it stays in this state until the junction is restored to its original, low-current state ("0") by sweeping the bias voltage to a negative threshold voltage ranging from approximately -7 to -8 V. The resistance changes by two orders of magnitude during this voltage sweep. This electrical switching of TCNQ-Cu has been explained as an electric-field-induced reversible redox reaction, which yields neutral Cu and TCNQ species from TCNQ-Cu and builds conduction channels in the material. These channels substantially increase the conductivity.^[21] Therefore, TCNQ-Cu nanowire-bridged electrodes hold promise for applications in high-density information storage as an organic electrical memory material due to the precise orientation and facile integration of the nanowires.

In conclusion, we have achieved the directed integration of TCNQ-Cu organic nanowires by a lateral bridging growth method, which allows for the reliable fabrication of devices by integrating TCNQ-Cu nanowires between prefabricated electrode structures. This method is simple and may be useful for the growth of TCNQ-Cu nanowires within devices at low temperatures on a variety of different substrates, including plastic surfaces. The directly grown nanobridge structure operates as a bistable electrical switch, demonstrating the potential of this technique. The fabrication method presented here represents a significant step towards the practical large-scale integration of high-quality organic nanostructures into high-density data storage devices and sensors.

Experimental

Fabrication of Electrodes: A highly doped (001) Si wafer with a 500 nm thick thermal-oxide SiO_2 layer was used as the substrate. Large pads were patterned on spin-coated photoresist by photolithography and Ti/Au metal layers were deposited on the patterned substrate. Small four-layer electrodes were patterned by electron-beam lithography and were connected to the large pads. Ti (20 nm), Au (50 nm), Cu (50 nm), and Au (100 nm) were sequentially deposited on the patterned substrate. The prefabricated electrodes with different gaps were formed after lift off.

Growth of TCNQ-Cu Nanowires: In general, TCNQ powders were loaded in a ceramic boat and the patterned substrate was placed on top of the ceramic boat with the patterned-electrode side facing down. The boat with the substrate was placed in a 2 in. quartz tube that was inserted into a tube furnace. The temperature of the furnace was increased to 120 °C and then maintained at that temperature for 2 h. Finally, the furnace was allowed to cool to room temperature. During the entire process, the argon gas flow rate was kept at 50–80 sccm.

Characterization: All the scanning electron microscopy (SEM) images were taken on a Hitachi S4700 field emission instrument operated at 10 kV. The Raman spectra of the TCNQ-Cu nanowires were recorded using a Renishaw 1000 confocal micro-Raman spectrometer with a laser excitation wavelength of 633 nm. The I - V curves of the nanowire devices were measured in air using a HP4156 semiconductor parameter analyzer linked to a probe station.

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