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Electrical Characterization of Si Microwires and of Si Microwire/Conducting Polymer Composite Junctions

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Supporting Information

Appendix A: Metallic Catalyst Removal Procedure

The silicon microwires were received as arrays grown on <111> silicon substrates.

Different samples were grown using both Au and Cu catalysts. The microwires were p-type doped with boron (using BCl_3) as the dopant. All the samples had the metallic catalyst on the end of each microwire and also have some minor amounts deposited on the sides. A slow cool down procedure has been done after growth so that the metallic catalyst diffuses out readily from the Si. The etch procedure for removing the catalyst and for etching off the SiO_2 that results from the catalyst removal is as follow:

10 s, 10% aq. HF

30 min. 30 wt.% aq. FeCl_3

10 s, 10% aq. HF

1 min 20 wt.% aq. KOH

10 s, 10% aq. HF

After each step, the microwires were rinsed thoroughly with DI water and dried under a stream of N_2 . FeCl_3 was used to remove the metallic catalyst. The KOH was used to remove any leftover FeCl_3 . Finally, buffered HF was used to remove the native oxide and any oxide formed during the catalyst removal process. XPS analysis confirmed the catalyst removal from the microwires after etching process (Figure A.1).

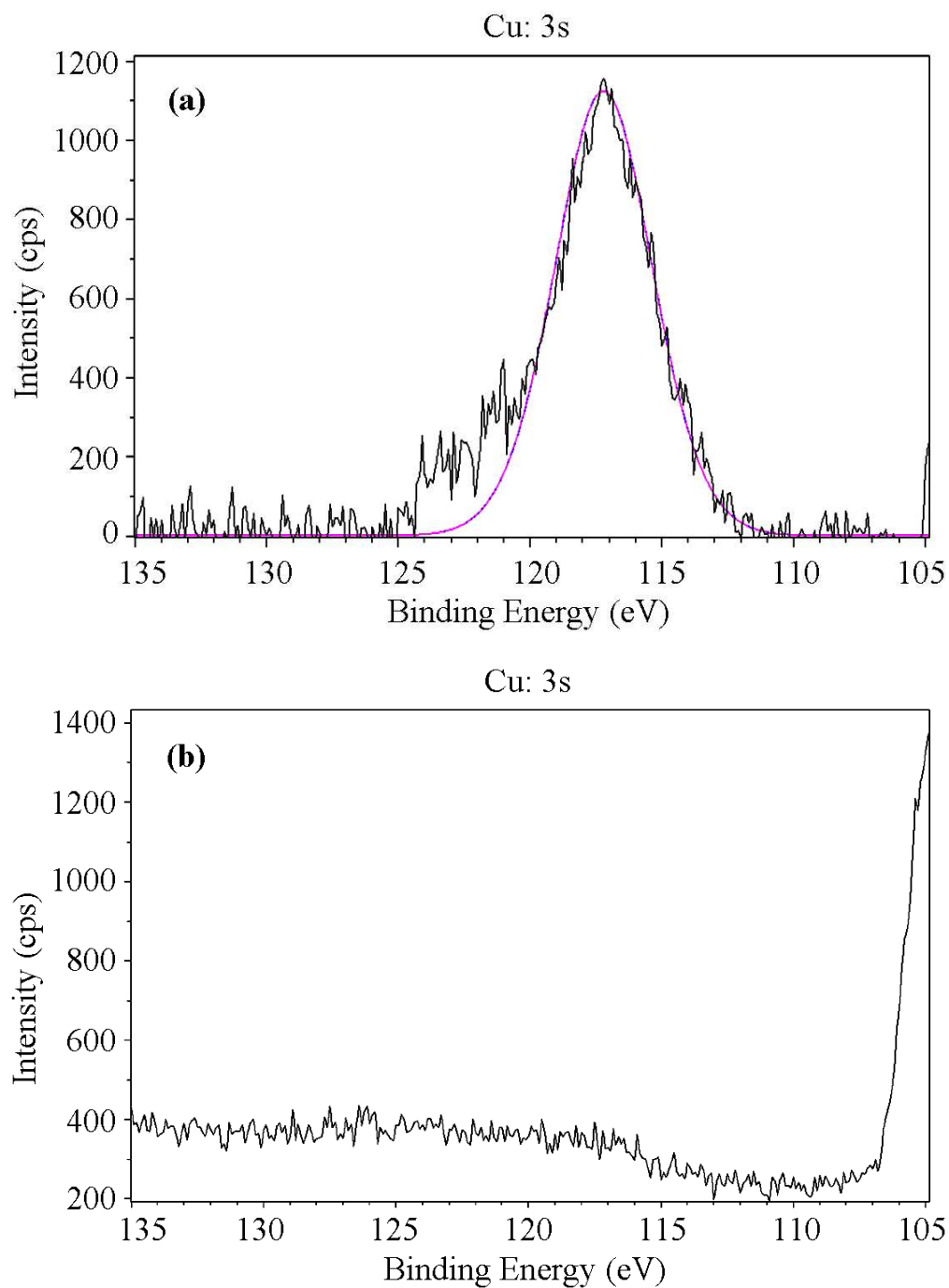


Figure A.1: XPS measurements (a) before and (b) after the etch process confirm metallic catalyst removal from copper-based microwires.

Appendix B: Conductive Polymer Film Preparation

B.1 Polymer Solutions

Two different conductive polymer solutions were prepared for the measurements. Each procedure includes the polymer solution preparation and spin coating the solution on the target substrates. The solution was coated at 2000 rpm for 20 seconds. The film preparation for each polymers followed by a rinsing process to remove the residual PSS or PMA.

Microwires were aligned before the rinsing process in all of the cases.

B.1.1 PEDOT:PMA

PEDOT:PMA solution was prepared using acetonitrile (CH_3CN) as the solvent. The procedure is as follows:

PMA solution: CH_3CN (1 mL) + PMA (1.09 g)

EDOT solution: CH_3CN (1 mL) + EDOT (42.6 μL)

These solutions were mixed and spin coated on the target substrates to form the final PEDOT:PMA membranes. For the rinsing process, the films were placed in dichloromethane (CH_2Cl_2) solution with a small amount of acetonitrile (3~4 mL) for ~ 30 min.

B.1.2 PEDOT:PSS:Nafion

PEDOT:PSS was purchased from Sigma Aldrich as a solution. In order to prepare 12 wt.% PEDOT:PSS:Nafion, 1250 mL of Nafion solution was mixed with 750 mL PEDOT:PSS and this solution was coated on the glass substrate. For the rinsing process, the films were placed in acetonitrile for ~ 30 min. following the rinsing process, the PEDOT:PSS:Nafion films were baked under vacuum at 100°C for one hour.

Appendix C: Microwire / Polymer Junction Formation

Following removal of the metallic catalyst (Figure C.1), and native oxide removal process (appendix A) a solution of microwires was prepared for coating on the target substrates by scraping a corner of the substrate using a razor blade and removing a smaller portion of the microwires. This is a desirable approach for single microwire measurements as the final solution was more diluted and, when coated on the substrate resulted in completely separated microwires. Single microwire measurements were performed by deposition of this solution ($\sim 10 \mu\text{L}$) onto an insulator substrate (e.g. glass). Direct contacts to the individual microwires were formed using tungsten probes and InGa in the probe station.

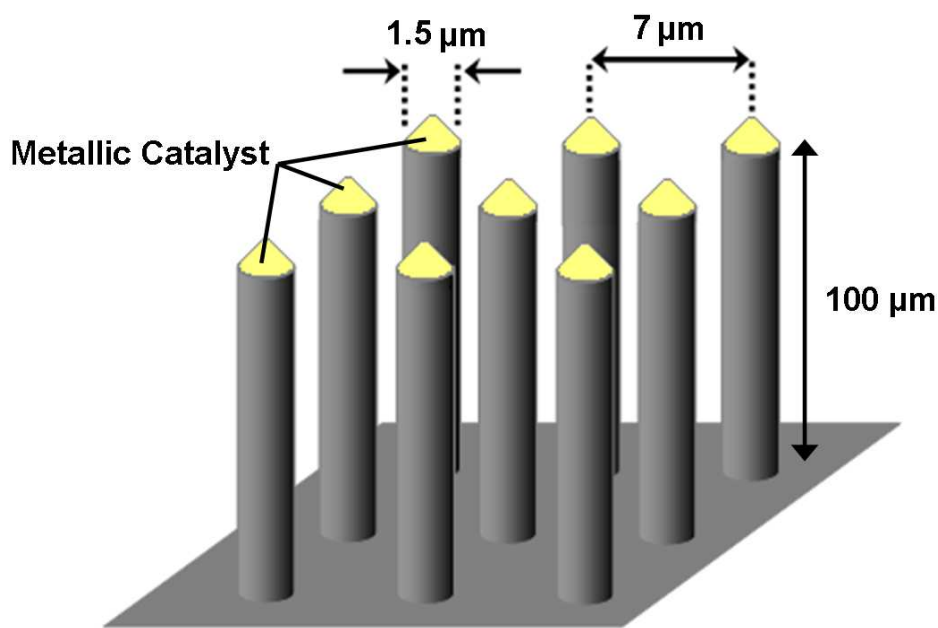


Figure C.1: Schematic diagram on the microwire arrays as received. The average diameter of the microwires is $1.5 \mu\text{m}$ and the array pitch size is approximately $7 \mu\text{m}$. the average length of the microwires is $100 \mu\text{m}$. The metallic caps are shown in yellow.

Tungsten probes are also etched using KOH before the measurements to remove the tungsten native oxide and improve the quality of the contacts. Using tungsten probes provides the ability to mechanically manipulate the microwires and make contacts to the individual wires as demonstrated in Figure C.2.

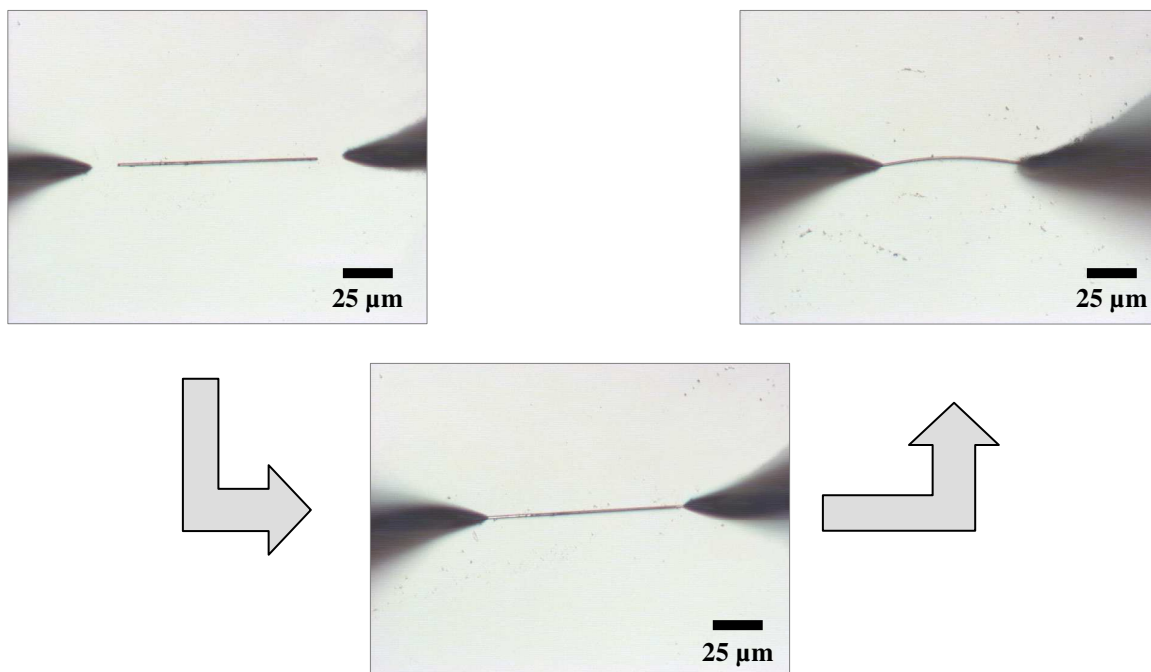


Figure C.2: Mechanical manipulation of silicon microwires using tungsten probes.

The probes were placed on both ends of the microwire and the current passing through the microwire was measured for a range of applied voltage using an *Agilent 4155c* semiconductor parameter analyzer.

Conductive polymer solutions, required for the microwire-polymer junction investigations, were prepared according to the established procedures (Appendix B). Ohmic contact to the conductive polymer was formed by sputtering gold directly on the polymer. The microwire solution (~10 μL) was deposited directly on the glass substrate after removing the paraffin tape. The next step was to align microwires at the border between the microwire and

conductive polymer in order to make electrical contact between the two elements. The schematic diagram of these measurements is shown in Figure C.3. Three important resistances in the system have been labeled in Figure C.3(c) as R_{polymer} , R_{contact} and R_{wire} which were going to be characterized.

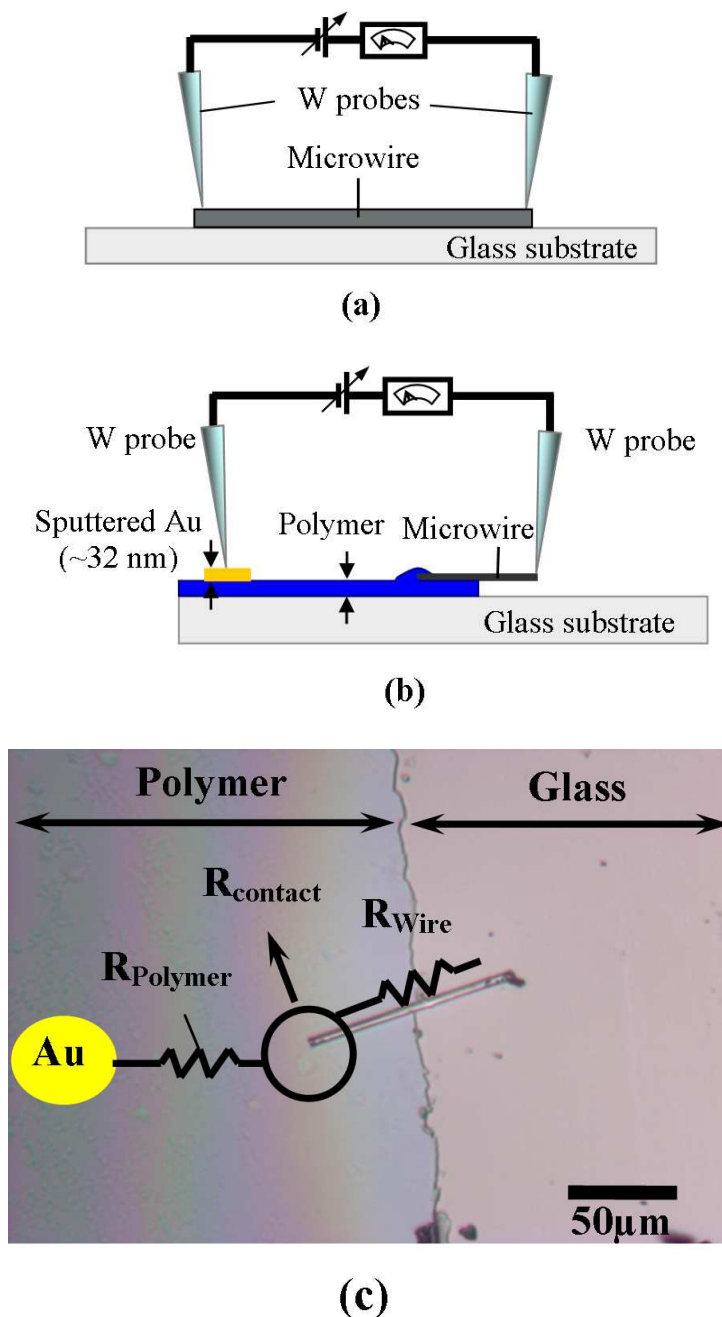


Figure C.3: Schematic diagrams for (a) single microwire measurements and (b) microwire/polymer junction characterization. The diameter of tungsten (W) probes is

approximately 1 μm . (c) an optical micrograph of a microwire aligned at the polymer/glass border with important resistances.

Appendix D: Quantifying the Applied Mechanical Force on the Single Silicon

Microwires

The required pressure to induce a phase transition in silicon is $\sim 112,000 \text{ kg.cm}^{-2}$ which is equal to $\sim 11 \text{ mN.}\mu\text{m}^{-2}$. The actual required pressure inducing such a transition in silicon microwires might be smaller considering the fact that the reported pressure in [19] was exerted on silicon indirectly through an interfacial layer (aluminum). Considering the weight of the probes ($\sim 0.2 \text{ g}$) and the contact area close to $1 \mu\text{m}^2$, based on the probe diameter, there is approximately $2 \text{ mN.}\mu\text{m}^{-2}$ applied to the microwire from the probes having no additional force applied to the probe.

However, to accurately determine the pressure applied by the probe to the Si microwire during the measurements, the force of the probe holder setup was measured using a balance. Placing the probe holder on a labjack adjacent to a tared balance the probe was lowered until the balance recorded a weight. The probe was then retracted until the balance returned to zero, this was taken as just touching the balance. From this point the probe was lowered a number of turns until a constant weight was achieved. After $3/4$ of a turn the weight stabilized at approximately 3.80 g . This is equivalent to 37.3 mN and given the probe's radius the applied pressure from this setup is $12 \text{ mN.}\mu\text{m}^{-2}$ which is enough to pass the required transition threshold.

We were able to observe the phase transition in the contacts by backing off the pressure on the microwires. Figure D.1(a) shows a measured I-V profile for a highly doped microwire with one probe fixed at one end of the wire with $\sim 37 \text{ mN}$ of force applied from the probe, and the second probe loosely connected to the other end with no additional force applied. Figure D.1(b) shows the change in the I-V profile as $\sim 37 \text{ mN}$ force was applied to the

second probe. This was a reversible procedure which repeated by increasing or decreasing the force on the probes.

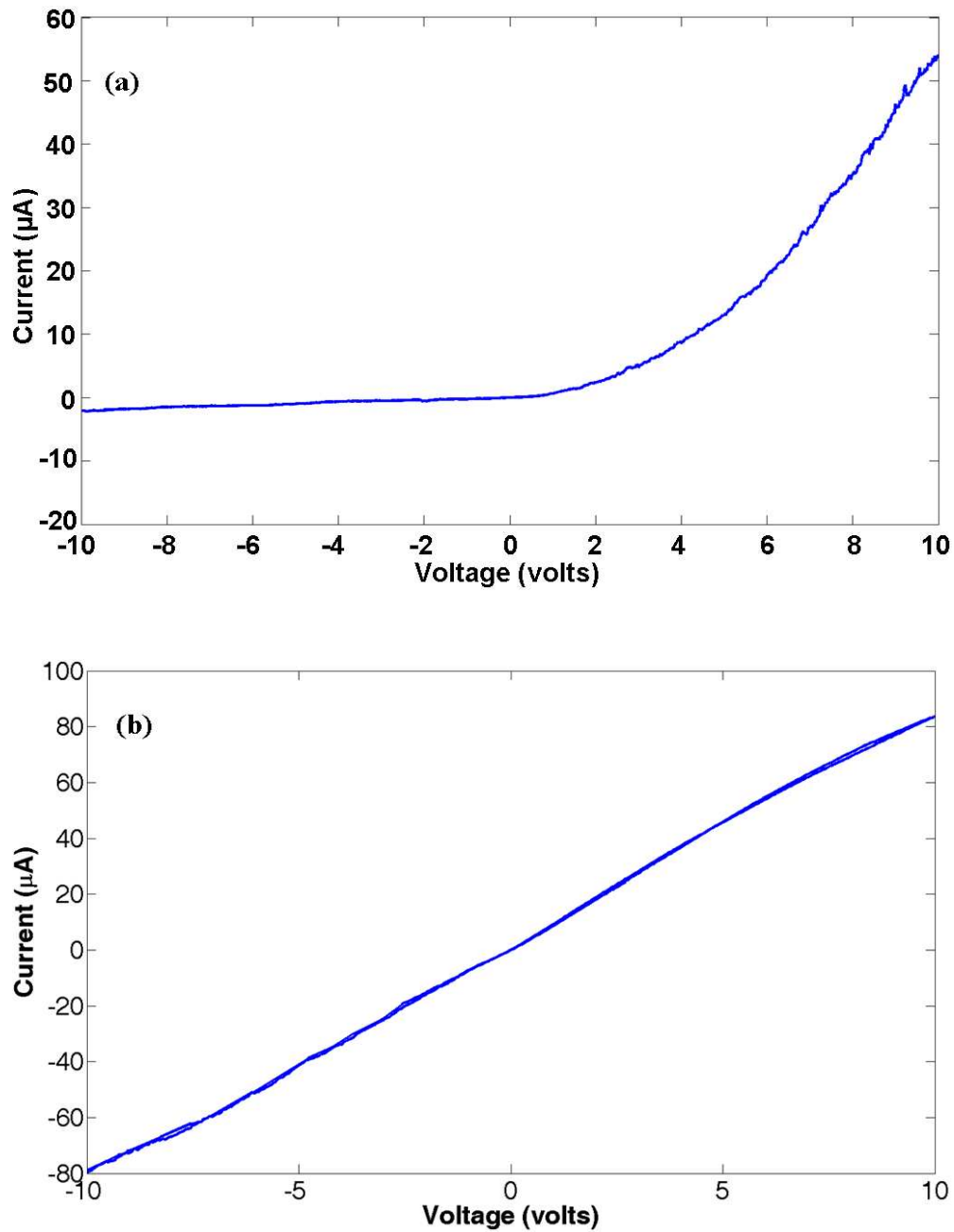


Figure D.1: Local phase transition as a result of pressure at the contact area can cause a change in the contact behavior. A highly doped $100\text{ }\mu\text{m}$ long microwire was investigated with the first probe fixed at one end of the wire (with $\sim 37\text{ mN}$ of applied force) while the second probe (a) touched the other end with almost no applied force to the probe (b) touched the other end with the same amount of force applied.