Supplementary Information for

Is Ballistic Transportation or Quantum Confinement Responsible for Changes in the Electrical Properties of Thin Polymer Films?

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Reagents

Selectophore Fluka reagents were used in this study: silver ionophore IV and sodium tetrakis [3,5-bis(triflouromethyl)phenyl] borate (NaTFPB). Analytical grade xylene was obtained from Chem-Supply (Port Adelaide, South Australia, Australia). Analytical grade KNO_3 was obtained from the Ajax Chemical Co. (Sydney, New South Wales, Australia). Similarly, analytical grade sulfuric acid and hydrogen peroxide used in piranha etching of silicon wafers were obtained from the Ajax Chemical Co. The monomers, 99.5% methylmethacrylate (MMA) and 99% n-decylmethacrylate (DMA), were obtained from Polysciences, Inc. (Gymea, New South Wales, Australia). The polymerization initiator, 98% 2,2-azobis(isobutyronitrile), was obtained from Sigma Aldrich (Castle Hill, New South Wales, Australia). Ethyl acetate and 1,4-dioxane were reagent grade and obtained from Chem-Supply. Milli-Q water was used in the preparation of all aqueous solutions unless otherwise specified.

Silicon Wafer Substrates

The doped and atomically flat silicon wafers [Si(100)] with dimensions of 8 cm in length, 4 cm in width and 2 cm in thickness were used as received as the working electrodes since they had been pre-polished to about 3 Å rms roughness [as obtained from Crystran LTD (Poole, Dorset, UK)]. The silicon was initially covered with 5-10 mm of excess xylene and placed on a hotplate at a temperature of 150 ^{o}C for 10 minutes. The wafer was rinsed with Milli-Q water prior to placement in a piranha etching solution for 10 minutes. Following the piranha etching process, a stream of ozone was passed over the silicon wafer surface to oxidize any extraneous organic material. The wafer was attached to the

spin coater, and rinsed with Milli-Q water at 3000 rpm before coating with copolymer films.

Preparation and Deposition of Ion Selective Electrode (ISE) Membrane

ISE membranes for X-ray reflectometry (XR) studies were prepared in a clean room. The piranha-etched wafers were subjected to spin casting, and the thin films were dried in a stream of high purity nitrogen gas prior to XR measurements.

PMMA-PDMA was synthesized using the method of Qin, Peper and Bakker[1] and thin films were prepared by spin-coating at 3500 rpm for 2 minutes with a solution of 98 wt% of PMMA-PDMA copolymer also comprising the silver ionophore (1.5 wt%) and NaTFPB (0.5 wt%), dissolved in appropriate quantity of xylene (0.3-1.5 % w/v) to give the desired film thickness. The PMMA-PDMA-coated wafers were annealed in a vacuum oven at 80 ^{o}C and 1.0 kPa overnight. Potassium nitrate solutions (1 M) were made up in Milli-Q water, and employed as the electrolyte in the EIS studies.

Electrochemical Impedance Spectroscopy (EIS)

EIS experiments were undertaken in a 1 M KNO_3 electrolyte using a custom-built cell (see Fig. S1). An anodised silver/silver chloride solid-state reference electrode was inserted into one of the inlet/outlet ports of the XR cell, a gold plate counter electrode was inserted into the other inlet/outlet port, and the silicon wafer working electrode were all connected to a Princeton Applied Research PARSTAT 2263 portable potentiostat. EIS experimental control and data acquisition were performed using a personal computer running the PowerSINE software, and EIS data were collected at the open circuit

potential using an A.C. amplitude of ±10 mV rms and a frequency range of 100 kHz–10 mHz.
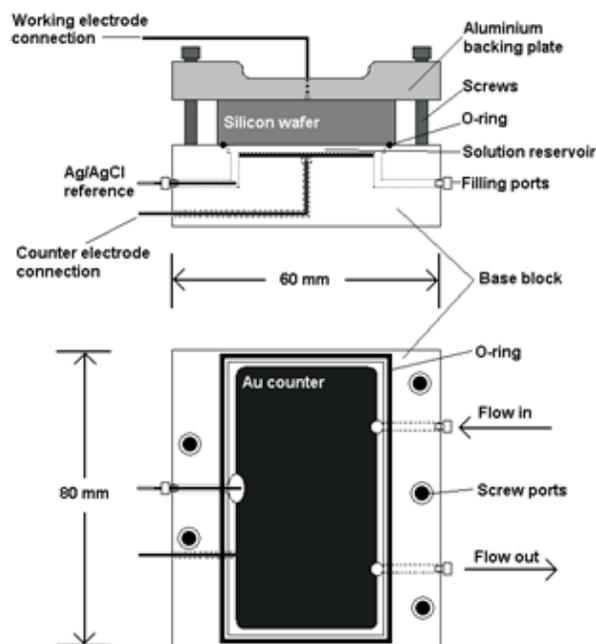
Fig. S1: Schematic diagram of the specialized cell used for the EIS experiments. Reproduced from Ref. *Analyst*, 2011, **136**, 3252 with permission from The Royal Society of Chemistry.

X-ray Reflectometry (XR)

XR was performed on the PMMA-PDMA coated wafers in air to ascertain the film thicknesses and roughness. X-ray reflectivity profiles were measured using a Panalytical Ltd X'Pert Pro Reflectometer using Cu Kα X-ray radiation (λ = 1.54056 Å). The X-ray beam was focused using a Göbel mirror and collimated with 0.1 mm pre-sample slit. The reflected beam was collimated before detection using parallel plate collimator.

Reflectivity data were collected over the angular range $0.05° \leq \theta \leq 3.00°$, with a step size of $0.010°$ and counting times of 15 s per step. Data were subsequently analysed using the MOTOFIT software package.[2]

Contact Resistance Considerations

Since the molecularly thin films had a tendency to be biased in the positive direction by a constant resistance in the system, especially as the film thickness diminished, we modelled the impact of a hypothetical 21 ohm contact resistance (a value yielding the approximate order of calculated electrical resistivity in these molecular thin films) at the silicon wafer/PMMA-PDMA interface. In this case, we linearly scaled the resistance (R) in the thin film using a bulk membrane resistivity (ρ) of 11 MΩ m, as measured independently using EIS and a macroscopically thick film.

$$R = \rho \left(\frac{l}{A} \right) \qquad\qquad \textbf{S1}$$

where l and A is the thickness and cross-sectional area ($\pi r^2 = 7.854 \times 10^{-3}$ m^2 for a 10 cm diameter silicon wafer) of the wafer.

Henceforth, $R_{apparent}$ is calculated as follows:

$$R_{apparent} = \rho \left(\frac{l}{A} \right) + 21 \qquad\qquad \textbf{S2}$$

and $\rho_{apparent}$ is calculated as follows:

$$\rho_{apparent} = R_{apparent} \left(\frac{A}{l} \right) \qquad\qquad \textbf{S3}$$

Fig. S2 presents an overlay of the actual resistivity data together with the apparent resistivity calculated using a constant contact resistance of 21 ohm.

Clearly, the absence of a deviation at high film thicknesses is expected since a 21 ohm contact resistance will not induce an offset in the bulk membrane resistance at values of tens to hundreds of MΩ. Even though the trends are very similar, the actual data displays a sharper and more abrupt change in resistivity, and the calculated data is biased significantly in both the negative and positive directions (i.e., a contact resistance cannot explain the results).
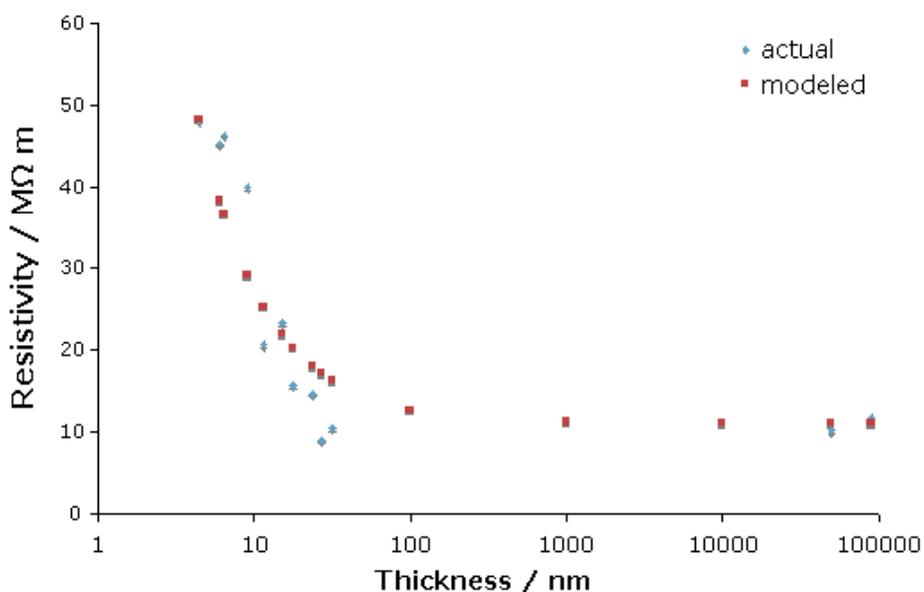
Fig. S2 An overlay of actual EIS resistivity and calculated resistivity by assuming a constant contact resistance of 21 ohm.

Reference

1   Y. Qin, S. Peper and E. Bakker, *Electroanalysis*, 2002, **14**, 1375.

2   A. Nelson, *J. Appl. Crystallogr.*, 2006, **39**, 273.