Supporting Information

Influence of the Contact Area on the Current Density across Molecular Tunneling Junctions Measured with EGaIn Top-Electrodes

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Experimental Details

Materials. Molecular precursors to all self-assembled monolayers (SAMs) were commercially available (≥ 98%, Sigma-Aldrich). All organic solvents were analytical grade (99%, Sigma-Aldrich) and were used as supplied. The *n*-alkanethiols were stored at 4°C to avoid degradation. To ensure that the compounds were free of contaminants, all stored compounds were checked by ^{1}H NMR prior to use.

Formation of SAMs of Decanethiol on Ag^{TS} Substrate. We formed SAMs on template-stripped silver (Ag^{TS})[1] substrates using solutions of thiolate (~3 mM) dissolved in anhydrous ethanol. The ethanolic solutions were purged with nitrogen before introduction of the metal substrate. The metal substrates were submerged in the solution of thiolate for 16-24 hours at room temperature and under an atmosphere of nitrogen. We rinsed the SAM-bound substrates with ethanol, and dried them under a gentle stream of nitrogen.

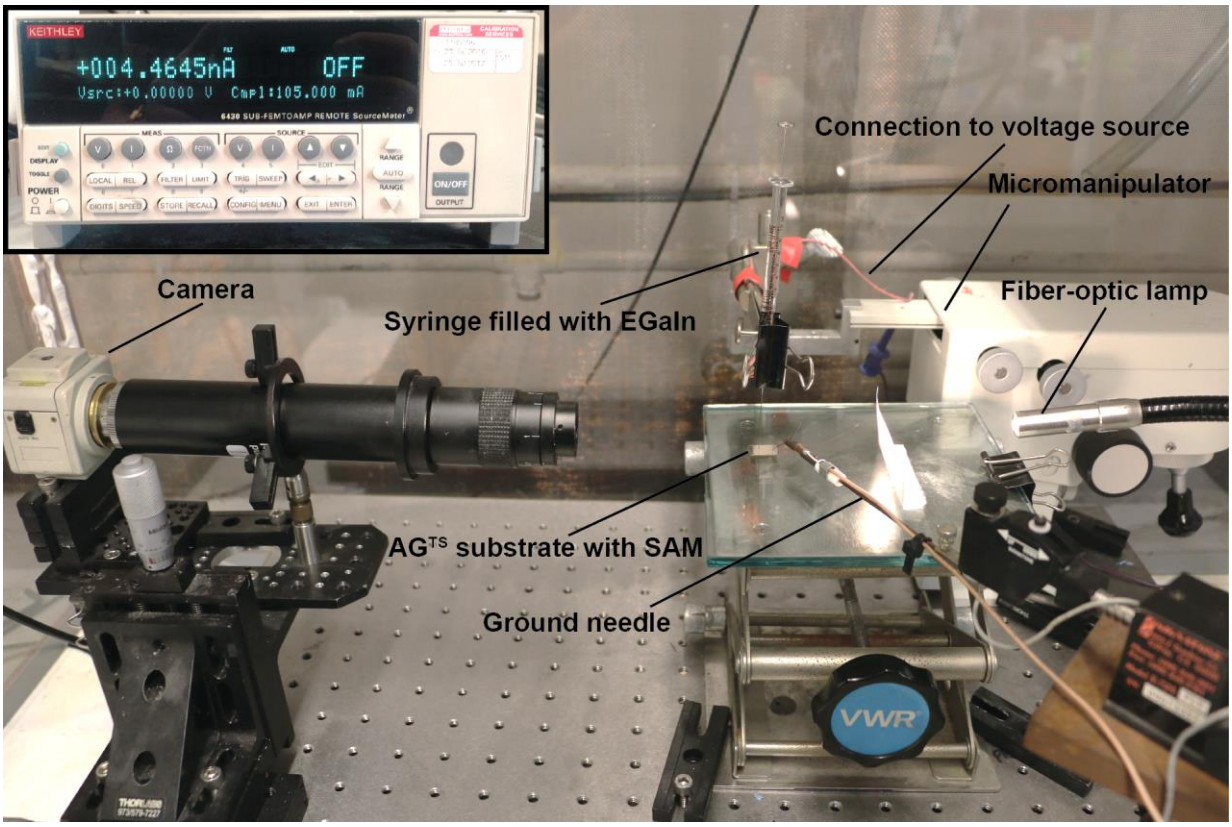

Figure S1. Image of the EGaIn Junction Station Used in the Measurements of $J(V)$. A syringe (Hamilton 1701 Gastight Syringe, 10 µL, Cemented, 26s gauge, 51 mm length blunt-tip needle) filled with EGaIn (Gallium-Indium eutectic, Aldrich 495425) is attached to a micromanipulator. Below the syringe lies a SAM bound to an Ag^{TS} substrate. The syringe needle is connected to a source-meter (Keithley 6430 Sub-Femtoamp Remote SourceMeter (SMU) Instrument/Electrometer, inset) with a cable, and the Ag^{TS} substrate is connected to the source-meter through a ground needle. For optical microscopy we use a CCD-camera (Resolution 640 x 480 px, magnification of objective 9x). A Fiber-optic light illuminates the EGaIn electrode from the back through a sheet of paper. The whole setup is placed on a vibration isolation table (Kinetic Systems, Vibraplane 2212-01-22). The experiments are performed in air and in a relative humidity between 20% and 40%.

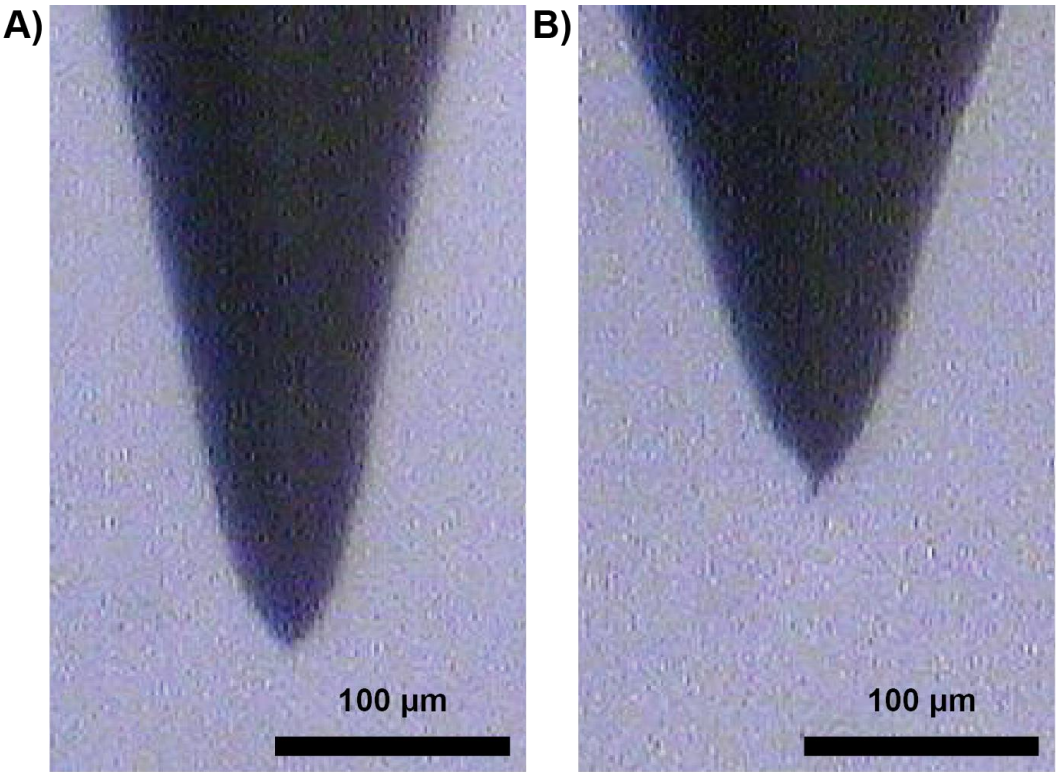

Figure S2. Images of two different EGaIn conical tip electrodes. We analyzed the surface of each newly fabricated EGaIn tip and selected only those that appear smooth by optical microscopy (A), and discarded tips with filaments present at the apex (B).

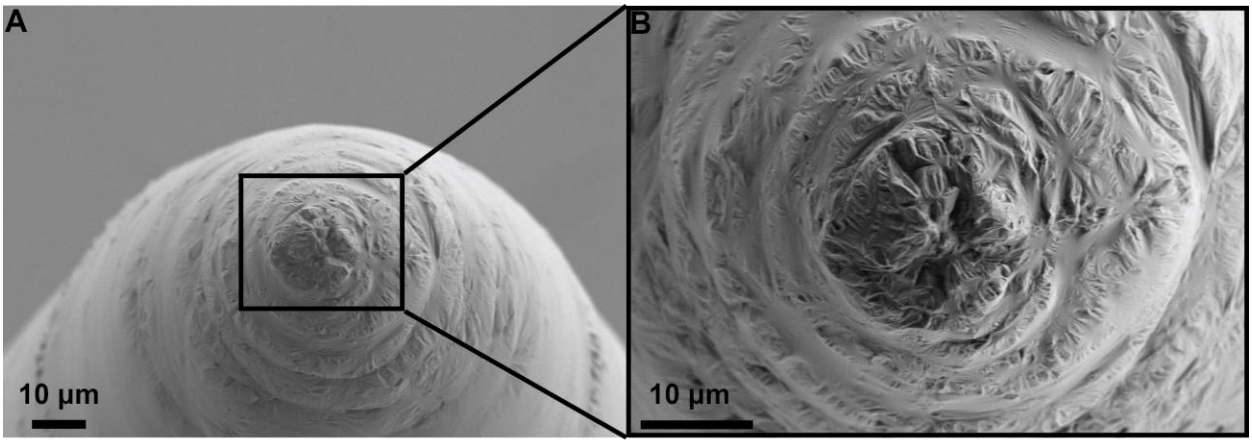

Figure S3. Scanning Electron Micrograph (SEM) of the apex of an upward facing EGaIn conical tip electrode. A) The apex of the electrode appears to be rougher and thicker than the sides. B) Magnified view of the apex of the conical tip. We expect the roughness of the downward facing tip used in the actual measurements of $J(V)$ to be smaller, because the skin has to support a small (~1 mm of EGaIn, ρ = 6.25 g/cm^3) column of liquid EGaIn.

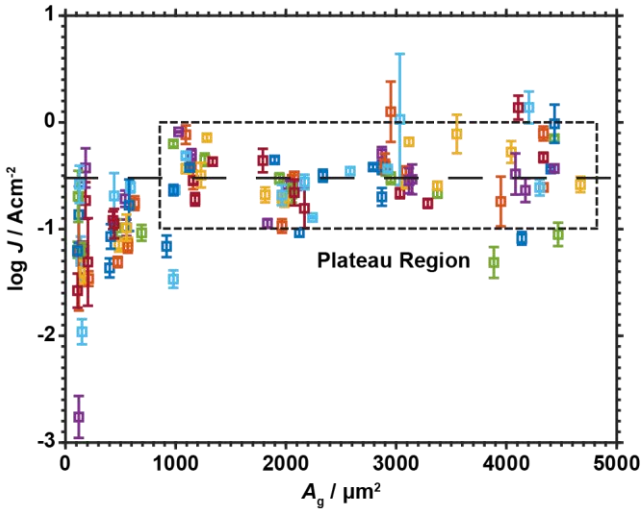

Figure S4. Current density of individual $Ag^{TS}/S(CH_2)_9CH_3//Ga_2O_3/EGaIn$ junctions at +0.5 V as a function of the geometric contact area of the junctions. We measured 20 *J-V* scans between -0.5 V and 0.5 V across each junction. The vertical error bars show the standard deviation of log *J* / Acm^{-2} measured with the junction. We formed each junction with a freshly fabricated tip. For $A_g < 1000\ \mu m^2$ the measured current densities are smaller, and more variable than in the plateau region ($1000\ \mu m^2 < A_g < 4300\ \mu m^2$).

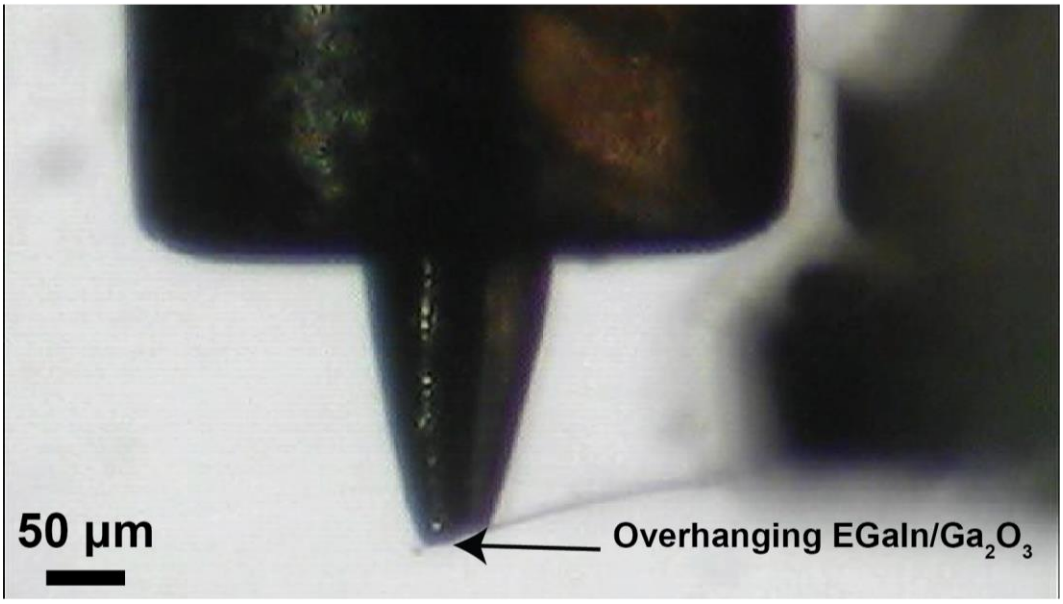

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Figure S5 Image of an EGaIn electrode contacting an AFM-cantilever. The diameter of the contact is larger than width of the cantilever, so that the conical tip hangs over the sides of the cantilever.

Mechanical model of the Gallium Oxide "Skin" on the Surface of EGaIn

Liquid EGaIn is a Newtonian fluid.[2] Unlike a classical liquid (*i.e.*, Hg, H_2O), EGaIn forms a thin (t ~ 0.7 nm) oxide layer in air, which stabilizes the EGaIn in shapes that are not governed by surface energy. Dickey *et al.*[2] measured the critical surface stress at which the oxide starts to yield or break in air ($\Gamma_{max} \sim 0.6$ N/m) allowing the EGaIn to flow (and immediately to be converted to oxide if exposed to air) by injecting it, under pressure, into a microfluidic channel. As opposed to the behavior of a classical liquid, EGaIn did not withdraw from the channel upon removal of the pressure; instead, the gallium oxide skin stabilized the EGaIn in the channel and prevented its withdrawal.

The effective shear stiffness of the oxide skin is $G_s \sim 13$ N/m,[2,3] measured using regular parallel plate rheometers. These experiments also showed that the mechanical behavior of Ga_2O_3/EGaIn can depend both on history and time.[3] The average thickness of the oxide in a stationary pool of EGaIn was determined to be t~0.7 nm using angle-resolved XPS.[4]

Even though the effective shear modulus of the skin of Ga_2O_3 ($G \sim 20$ GPa) is comparable to that of Aluminum (G ~ 30 GPa), its average thickness (~0.7 nm) is 10^{-5} smaller than the diameter of the tip (~0.1 mm), which allows the tip to conform to the bottom-electrode on a scale that we can observe with optical microscopy.

We approximate the oxide skin on the EGaIn conical tip as a thin-walled pressure vessel (Figure S6). Let Γ_h (N/m) be the hoop force per unit length and Γ_a (N/m) be the axial force per unit length. Let p_h be the hydrostatic pressure from the EGaIn inside the conical tip, and p_n be the nominal pressure acting on the bottom electrode. Because the skin is thin compared to the diameter of the tip ($t/D \sim 10^{-5}$) it can be treated as an elastic membrane that cannot sustain compressive stresses, and starts to wrinkle under compressive loads, an effect that we can

observe in our experiments (Video S1). This observation allows us to neglect Γ_a in a force balance close to the contact in vertical direction (Figure S6B) and we obtain a relationship (eq. S1) between p_h and p_n.

$$p_h = p_n \tag{S1}$$

From the force balance on of a slice of oxide skin cut in vertical direction (Figure S6B) we obtain eq. S2.

$$p_h = \Gamma_h D^{-1} \tag{S2}$$

Combining equations (S1), (S2), and (3) gives us the functional form (S3) that was observed in the measurement of the nominal contact pressure on AFM-cantilevers (Figure 6).

$$p_n = \Gamma_h (A_g/\pi)^{-0.5} \tag{S3}$$

Fitting the data to eq. S3 gives $\Gamma_h = 0.1$ N/m. This value is on the same order of magnitude than the maximum possible value of $\Gamma_{max} \sim 0.6$ N/m measured by Dickey *et al*..[2]

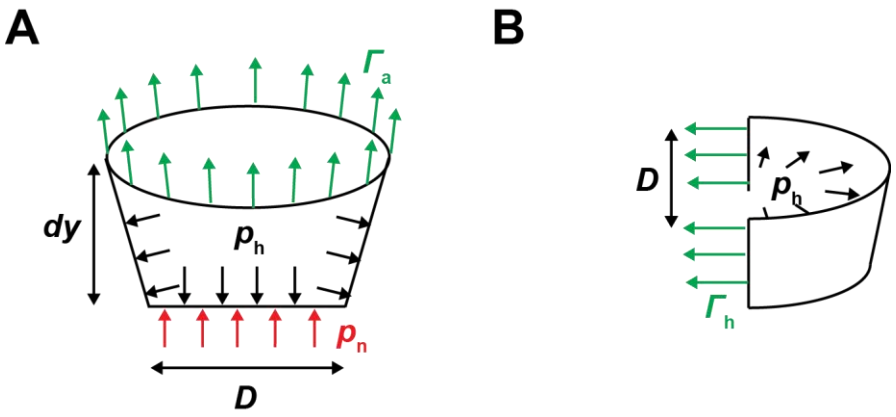

Figure S6. Free-body diagrams with estimated forces in the oxide skin. A) Cut parallel to the contact of the cone to calculate the longitudinal stress B) Additional cut parallel to the axis to calculate the hoop force inside the membrane.

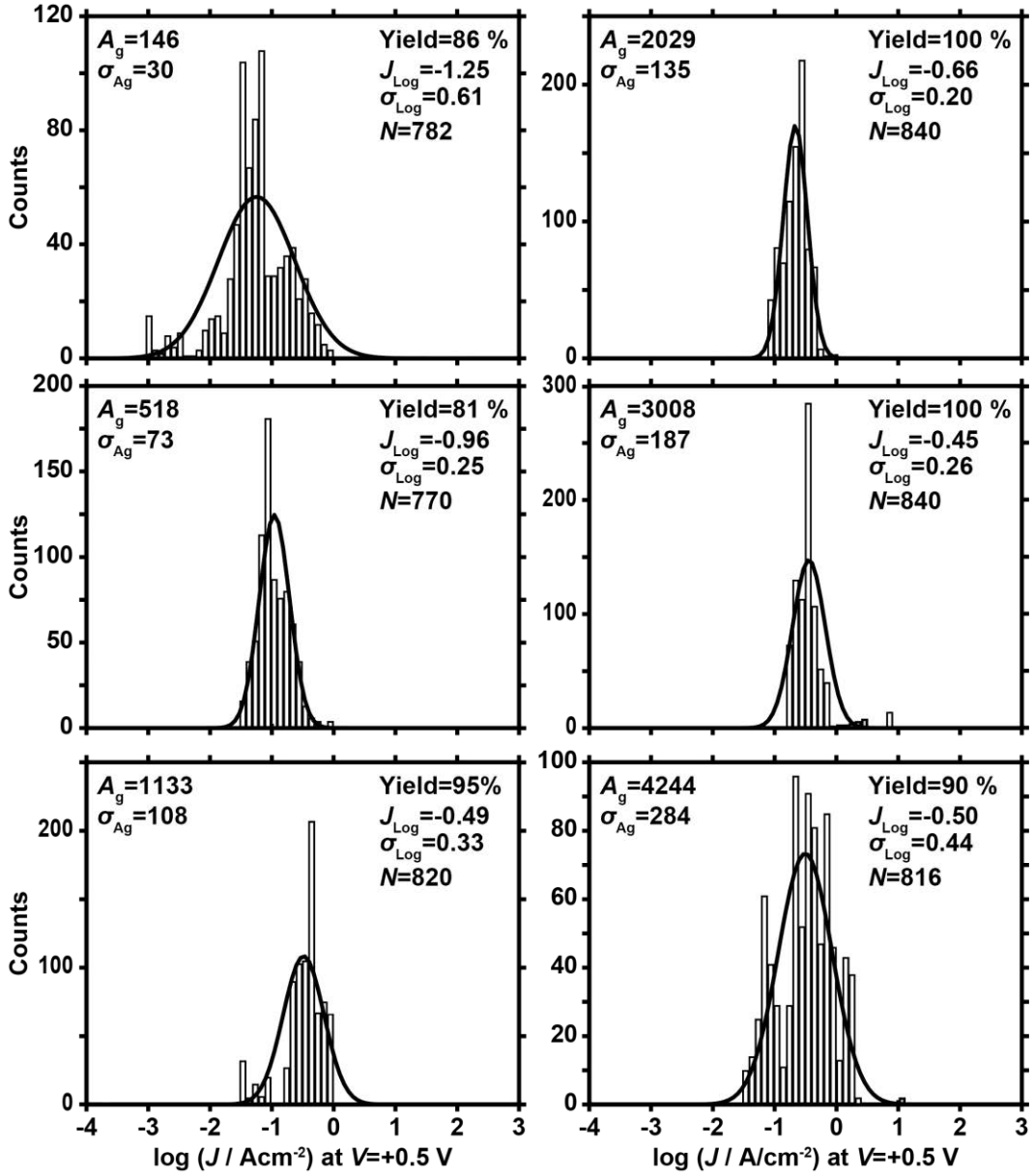

Figure S7. Histograms of log (J/(A/cm^2)) at + 0.5 V across $Ag^{TS}/S(CH_2)_{10}//Ga_2O_3/EGaIn$ junctions for sets of data collected with different geometric contact areas (mean contact area A_g (μm^2), standard deviation σ_{Ag} (μm^2)). Solid curves indicate a Gaussian fit with mean value J_{Log} and standard deviation to σ_{Log} to the histograms and N indicates the number of data point used in the fit. The yield is the percentage of junctions that did not short after the first voltage sweep between -0.5 V and +0.5 V.

References

(1) Weiss, E. A.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Schalek, R.; Whitesides, G. M. Si/SiO_2-Templated Formation of Ultraflat Metal Surfaces on Glass, Polymer, and Solder Supports: Their Use as Substrates for Self-Assembled Monolayers. *Langmuir* **2007**, *23*, 9686–9694.

(2) Dickey, M. D.; Chiechi, R. C.; Larsen, R. J.; Weiss, E. A.; Weitz, D. A.; Whitesides, G. M. Eutectic Gallium-Indium (EGaIn): A Liquid Metal Alloy for the Formation of Stable Structures in Microchannels at Room Temperature. *Adv. Funct. Mater.* **2008**, *18*, 1097–1104.

(3) Larsen, R. J.; Dickey, M. D.; Whitesides, G. M.; Weitz, D. A. Viscoelastic Properties of Oxide-Coated Liquid Metals. *J. Rheol.* **2009**, *53*, 1305.

(4) Cademartiri, L.; Thuo, M. M.; Nijhuis, C. A.; Reus, W. F.; Tricard, S.; Barber, J. R.; Sodhi, R. N. S.; Brodersen, P.; Kim, C.; Chiechi, R. C.; Whitesides, G. M. Electrical Resistance of Ag^{TS}–$S(CH_2)_{n-1}CH_3$//Ga_2O_3/EGaIn Tunneling Junctions. *J. Phys. Chem. C* **2012**, *116*, 10848–10860.