The Electrical Resistance of

Ag^{TS}-$S(CH_2)_{n-1}CH_3$//Ga_2O_3/EGaIn Tunneling Junctions

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Supporting Information

Methods

Procedure to Make Tips. We generated tips (n = 14) (in a fumehood, in the ambient atmosphere, and at room temperature), by the four-step procedure described earlier[1] and summarized in Figure 1; this procedure took ~30 min. i) We formed a droplet at the tip of a syringe needle; ii) we compressed the droplet against a SiO_2/Si substrate placed on top of a vertically translatable stage until it adhered. iii) We lowered the stage away from the syringe. The droplet extended into a thin bridge of EGaIn. Upon reaching a certain extension, the bridge ruptured, and left two sharp tips, one projecting upwards from the substrate and the other projecting downwards from the syringe. The radius of curvature at the tip was ~100 μm for all our samples.

Procedure to Make Deformed ("Cycled") Tips. A total of seven tips were deformed repeatedly for 25 times by gently pushing the two opposing tips against each other. The contact and deformation of the two tips was verified by using a microscope. The tip pointing upward was the one characterized by XPS and ToF-SIMS.

Procedure to Make Drops. A large droplet (~10 mm in diameter, ~2 mm in thickness) of Ga_2O_3/EGaIn was deposited onto a Si/SiO_2 wafer subtrate (used as received) with a Pasteur pipette. By using the focus distance of the optical microscope within the XPS, we identified the topmost spot of the interface between Ga_2O_3/EGaIn and air. We collected XPS spectra from that spot, to provide a control sample with low surface curvature.

Angle-Resolved XPS. Angle-resolved XPS was collected using a Thermo Scientific Theta Probe located at the University of Toronto. Initial work was performed on several tips formed as described above. Initial survey spectra at low-energy resolution (pass energy – 200 eV) were

obtained on the tips using the standard analysis mode (i.e. angles summed over 60° angular acceptance). A spot size of 100 μm was used. Low energy resolution spectra were obtained also for the Ga 2p3/2, In 3d, O 1s, C 1s and Ga 3d / In 4d regions in the ARXPS mode (8 angles). A snapshot mode was used with a pass energy of 200 eV. Higher energy resolution spectra were obtained for the Ga 2p3/2 and Ga 3d/In 4d spectral regions. In this case the spectra were collected in a scanned mode (pass energy - 50 eV) and 6 angles were utilized.

The experiment was repeated on a large drop which allowed use of a larger spot size (400 μm). This enabled ARXPS data to be collected over 16 angles with statistics adequate to perform the maximum entropy calculations. We assumed that the radius of curvature would be large enough for ARXPS to be valid; any effects contributed by the curvature would be cancelled out as the Theta Probe obtains its angular information in a parallel mode without the need to tilt the sample.

To obtain accurate chemical shifts between the Ga 3d/In 4d species, high energy resolution spectra were obtained on this spectral region using a Thermo Scientific K-Alpha XPS also situated at the University of Toronto. The spectra were obtained on a large drop. As with the Theta Probe, a 400 μm spot size was used. The photoelectrons emitted were collected normal to the surface. A pass energy of 5 eV was used. Fitting was performed utilising the software provided with the instrument (Avantage) and the parameters obtained were applied to the ARXPS spectra obtained on the Theta Probe. As with the K-Alpha, all data processing on the Theta Probe was performed using Avantage.

All assignments were made consistently with literature values.[2] The gallium species are represented in Figure 2a by four peaks. The doublet at a binding energy of ~18.2 eV originates from the Ga 3d5 and Ga 3d3 orbitals of metallic gallium. The peak at ~20.5 eV was assigned to

Ga$_2$O$_3$ species. We assigned the remaining peak at ~19 eV to Ga^{1+} species, plausibly representing a gallium suboxide. An XPS signature of monovalent gallium was already claimed by Scharmann et al. in their analysis of the oxidized surface of a Ga-In-Sn eutectic.[3] We did not deconvolute the Ga^{1+} and Ga^{3+} peaks into their 3d5/2 and 3d3/2 components since no interference from In peaks is expected at those high (>19 eV) binding energies.

The assignments were further confirmed by measuring the high resolution spectrum of the Ga 2p and O 1s regions from a Ga$_2$O$_3$/EGaIn drop sample (Figure S1 in the Supporting Information). The Ga 2p spectrum has the advantages of i) not overlapping with In peaks and of ii) not displaying spin-orbit splitting. The spectrum could only be deconvoluted by using three peaks, representing Ga^0, Ga^{1+}, and Ga^{3+}. The O1s spectrum also indicated the presence of three species: inorganic oxides (at 530.8 eV, labeled O1s), and two other kinds of oxygens (at 531.5 eV and 532.8 eV, labeled O1s A and O1s B) assigned respectively to chemisorbed water or surface hydroxyls and to oxidized carbons.

The indium species are represented in Figure 2a by four peaks representing two species. The first doublet at ~16.3 eV and ~17.3 eV is attributed to In^0, according to literature values. The second doublet, weaker and at higher binding energy (~17.1 eV and ~18 eV), was instead attributed to In$_2$O$_3$, after a positive comparison with the spectrum obtained from the In$_2$O$_3$ standard.

ToF-SIMS. All of the ToF-SIMS experiments described here were conducted on SI-Ontario's ToF-SIMS IV tool (ION-ToF Gmbh., Munster, Germany). In all cases, we acquired the depth profiles using a dual –beam approach. A Ga$_2$O$_3$ thin film on silicon with a known thickness (50 nm) was used to calibrate the sputtering rate. The analysis beam was 25 keV Bi^{1+}, operated in high-spectral-resolution bunched mode. The analysis beam-current was 1.0 pA. In each case,

we used an analysis area of ~50x50 µm^2. In order to generate the sputter craters, we used low energy (500 eV) argon ions, a current of ~4.5 nA (we measured the exact current for each profile) over an area of 200x200 µm^2. The analysis area lies at the center of the sputter crater. Secondary ion images were performed with the machine operating in an unbunched imaging mode. Bi^{3+} ions were used for imaging. Secondary electron images were acquired by operating the machine in a low-current, small-spot (>100 nm) mode. Secondary electrons were acquired rather than secondary ions. The samples had to be frozen before characterization. Islands of oxide detached from the oxide film as the surface of the sample was sputtered. When the metal below the oxide was liquid, these islands floated and moved towards the apex of the drop (Ga$_2$O$_3$ is less dense than EGaIn), intercepting the analysis beam and compromising the measurement. The solidification of the drop, while necessary for the characterization, is expected to introduce roughness in the surface of the material: the liquid eutectic has in fact a larger thermal expansion coefficient than the oxide. The ToF-SIMS analysis of a thin film of Ga$_2$O$_3$ of known thickness allowed us to i) calibrate the sputtering rate (namely, to measure the number of nanometers sputtered every minute from Ga$_2$O$_3$ in a specific set of sputtering conditions), and ii) to identify the most abundant fragments (^{69}GaO, ^{71}GaO, ^{69}GaO$_2$, ^{71}GaO$_2$) ejected from the surface of Ga$_2$O$_3$ during sputtering.

Supplementary Definitions and Discussion

Ag^{TS}-S(CH$_2$)$_{n-1}$CH$_3$//Ga$_2$O$_3$/EGaIn tunneling junctions. These tunneling junctions comprise three principal components: (i) the SAM, (ii) the template-stripped Ag (Ag^{TS}) substrate and "bottom" electrode, and (iii) the Ga$_2$O$_3$/EGaIn "top" electrode. *Thiolate SAMs.* Self-assembled monolayers of alkanethiolate should, in principle, be good model systems to use in physical-

organic studies of charge transport across molecules. When the starting alkanethiols are carefully purified, SAMs of alkanethiolates have three important qualities: (i) a molecular structure that is precisely controllable and well defined, (ii) a reasonable stability (typically days) in ambient conditions, (iii) a thickness (defined by the structure of the alkanethiol, the structure of the SAM, and the topography of the Ag^{TS} surface) that is defined with an accuracy of ±10%.[4,5] *Ag^{TS} Substrates*. Silver is a good substrate for the characterization of charge transport through SAMs of alkanethiolates. The packing density of alkanethiolate in a SAM on flat Ag substrates is 26% higher than on flat Au substrates due to differences in the tilt angle (10º on Ag vs. 30º on Au) of the alkanethiolate molecules in the SAM and in the footprint of the thiolate on the two metals.[6,7] Template-stripped Ag substrates (Ag^{TS}) have a lower root-mean-square roughness (1.2 ± 0.1 nm) than do Ag substrates (Ag^{AS-DEP}) deposited by an electron-beam evaporator (5.1 ± 0.4 nm). A flatter substrate should introduce fewer defects into the structure of the SAM. Defects in the structure of the SAM are considered one of the causes of shorts in tunneling junctions based on SAMs;[8] a flatter substrate should, therefore, result in fewer shorts. Previous work from our laboratory supports this hypothesis: junctions formed on Ag^{AS-DEP} substrates failed 3.5 times more frequently than those formed on Ag^{TS} substrates.[9] *Ga_2O_3/EGaIn "Top" Electrode*. Electrodes made of Ga_2O_3/EGaIn are useful in SAM-based tunneling junctions for three reasons. (i) The bulk EGaIn alloy conducts electricity as a metallic conductor (the conductivity of bulk EGaIn is ~10^6 S·m^{-1}; for comparison, the conductivity of Al is 10^7 S·m^{-1}). (ii) Ga_2O_3/EGaIn has the apparent rheological behavior of a shear-yielding fluid; it flows under moderate surface-shear stresses (0.5 N·m^{-1}), but retains its shape when the stress is removed.[1,10,11] Therefore, Ga_2O_3/EGaIn can retain sharply curved, yet compliant features (i.e., conical tips) that can form small-area (~100 μm^2), nondestructive contacts when brought into gentle contact with the

surface of SAMs. (iii) The (apparently) self-limiting, flexible, but incompressible skin prevents the formation of metal filaments through the SAM (or its defects); the formation of filaments is the most common cause of shorts in junctions formed with evaporated metal top electrodes.[12]

Advantages of Ga₂O₃/EGaIn electrodes. As a top electrode in SAM-based molecular junctions, Ga_2O_3/EGaIn offers four useful characteristics (Table I). *Throughput and Yield of "Working" Junctions*. The Ag^{TS}-SR//Ga_2O_3/EGaIn junctions are sufficiently easy to fabricate and use that they allow the collection of statistically significant numbers (N = 400-800) of *J(V)* traces from relatively large numbers (20-40) of junctions in convenient times (~1 day). "Working" junctions (i.e., in the case of junctions comprising SAMs of alkanethiolates, those junctions whose *I-V* curves are evidence that charge transport through the junction is dominated by a tunneling mechanism) are routinely formed with yields that are >70% and that depend on the structure of the thiol comprising the SAM.[13-15] The statistically significant number of *J(V)* traces obtained from these junctions results in distributions of log*J(V)* values that can be adequately fitted to Gaussian distributions.[16] The accuracy of this fitting procedure allows us to calculate the values of log*J(V)* with a relative uncertainty as small as 0.08. *Toxicity*. Ga_2O_3/EGaIn is non-volatile and less toxic than the Hg used in "Hg drop" junctions. *Requirements for Instrumentation*. The preparation of the samples, and the collection of the *J(V)* curves from Ag^{TS}-SR//Ga_2O_3/EGaIn junctions, do not require a controlled atmosphere or vacuum, or equipment that is either expensive or sophisticated (e.g., a clean room). They do, however, require an experienced operator[17] (a caveat that is not unique to this technique[18]). *Impact on SAM*. The formation, characterization, and use of Ag^{TS}-SR//Ga_2O_3/EGaIn junctions do not appear to destroy, or interfere with, the structure of the SAM[19] (as shown for evaporated metal junctions,[12] and suspected for large-area PEDOT:PSS-based junctions[20]).

Adsorption of Water Vapor on Surfaces. The adsorption of water on surfaces in the ambient atmosphere is affected by temperature, relative humidity, reactions between water and the surface (e.g. chemisorption onto oxide surfaces), the roughness and curvature of the surface, competition with the adsorption of adventitious organic contaminants, the duration of exposure to water vapor, and defects or impurities at the surface. Due to its complexity, the adsorption of water on surfaces is typically studied in conditions that can simplify its understanding (e.g. HVAC, low temperatures), but that are very different from ambient atmosphere. These studies give us limited information about the quantitative details of water adsorption (e.g., the amount of water adsorbed and its distribution) in conditions that are meaningful for our study. Studies at ambient pressures and temperatures are more meaningful to our study and have compared data (e.g., adsorption isotherms) obtained by gravimetry[21], IR spectroscopy[22], and Ambient Pressure XPS (APXPS)[23,24] on surfaces of polar (e.g., quartz, borosilicate glass, Cu, TiO_2) and nonpolar surfaces (e.g., PTFE, n-octyltrichlorosilane SAMs on Si). The adsorption of water at high RH (>75%) was reported to be quite sensitive (ranging from four to eight layers of water) to the history and composition of the surface.[22] At lower RH (between 20% and 60% RH), instead, the amount of water adsorbed (usually ~two water layers) was independent of the processing history of the surface and consistent across techniques (i.e., gravimetry, IR spectroscopy, and surface conductivity).[21-24]

Adsorption of Organic Vapors on Surfaces. All surfaces (e.g., metals, such as EGaIn, and salts, such as Ga_2O_3) adsorb some adventitious species (e.g. water, CO_2, CO, O_2, volatile organics, fatty acids, ions, hydrocarbons, sulfur-containing molecules, dust particles, and aerosols) when exposed to ambient conditions;[25] the rate of deposition depends on the surface energy, the reactivity of the adsorbate, and the partial pressure of contaminants in the

atmosphere. Ga_2O_3/EGaIn tip electrodes are exposed to the laboratory atmosphere for a few minutes during the formation of Ag^{TS}-SR//Ga_2O_3/EGaIn junctions. We must, therefore, consider the possibility that adventitious contamination of the surface of the tip affects the $J(V)$ measurements obtained from the junctions. This complication is not unique to our technique, but should be accounted for in all techniques in which any element of the molecular junction has been exposed — during fabrication, use, or storage — to ambient atmosphere. Therefore, an analysis of the impact of adventitious contamination on the resistance of Ag^{TS}-SR//Ga_2O_3/EGaIn junctions is relevant to most experimental efforts in molecular electronics.

Adventitious organic contaminants originate from a multitude of sources: photooxidation of volatile organic molecules, plasticizers, breath, curing agents, plant debris, dead skin, tapes, gloves, clothes, oils and greases, etching solutions, solvents, mold releases, body oils, cosmetics, food, rubber fragments, etc…[26-28] Their composition is different from place to place, and from time to time. Nonetheless, the collective body of work performed with XPS suggests that adventitious carbon is characterized by six features:[25,29] (i) it is not homogeneously distributed on the surface; (ii) it is detected in every sample that is prepared in ambient atmosphere; (iii) its physical and chemical properties are similar from sample to sample; (iv) it is chemically closer to hydrocarbons than to graphitic carbon; (v) it is not covalently bound to the surface; (vi) it does not necessarily originate from pump oil in the vacuum system of the XPS. Analyses conducted with other techniques (e.g., AFM) showed that these contaminants are mobile,[30,31] they partially desorb under vacuum,[30] they can react with the water adsorbed at surfaces,[32] they can segregate atop water droplets,[30-32] and they can reduce the work function of the surface on which they are adsorbed by ~1 eV.[33,34] The rate of deposition of adventitious organic contaminants on surfaces has been reported to vary by orders of magnitude, depending on the conditions (we found reports

of rates between 0.001 nm/day[35] to 0.4 nm/h[36] for laboratory environments), to decrease quickly

with increasing coverage,[37] and to be higher at defects or grain boundaries.[31] The distribution of

adventitious contaminants on surfaces (including that of Ga_2O_3/EGaIn) is still unclear. However,

scanning probe microscopy experience and published reports[30,31], XPS experience,[25,38] and the

rates of adsorption measured by other techniques (e.g., thermodesorption-gas

chromatography/mass spectrometry)[37,39] consistently suggest that organic contaminants do not

form a continuous layer on initially-clean surfaces within the timeframe of typical usage of a

Ag^{TS}-SR//Ga_2O_3/EGaIn junction (~20 min)

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