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Environmental Influences on the Measurement of Rates of Charge Transport across $Ag^{TS}/SAM//Ga_2O_3/EGaIn$ Junctions

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ABSTRACT

This paper investigates the influence of the atmosphere used in the fabrication of top-electrodes from the liquid eutectic of gallium and indium (EGaIn) (so-called "EGaIn" electrodes), and in measurements of current density, *J*(V), across self-assembled monolayers (SAMs) incorporated into AgSR//Ga_2O_3/EGaIn junctions, on values of *J*(V) obtained using these electrodes. A gas-tight measurement chamber was used to control the atmosphere in which the electrodes were formed, and also to control the environment in which the electrodes were used to measure current densities across SAM-based junctions. Seven different atmospheres—air, oxygen, nitrogen, argon, and ammonia, and air containing vapors of acetic acid and water—were surveyed using both "rough" conical-tip electrodes, and "smooth" hanging-drop electrodes. (The manipulation of the oxide film during the creation of the conical-tip electrodes leads to substantial, micron-scale roughness on the surface of the electrode, the extrusion of the drop creates a significantly smoother surface). Comparing junctions using both geometries for the electrodes, across a SAM of *n*-dodecanethiol, in air, gave $\log|J|_{mean} = -2.4 \pm 0.4$ for the conical tip, and $\log|J|_{mean} = -0.6 \pm 0.3$ for the drop electrode (and thus $\Delta\log|J| \sim 1.8$); this increase in current density is attributed to a change in the effective electrical contact area of the junction. To establish the influence of the resistivity of the Ga_2O_3 film on values of *J*(V), junctions comprising a graphite electrode and a hanging-drop electrode were compared in an experiment where the electrodes did, and did not, have a surface oxide film; the presence of the oxide did not influence measurements of log |*J(V)*|, and therefore did not contribute to the electrical resistance of the electrode. The presence of an oxide film did, however, improve the stability of junctions, and increase the yield of working electrodes from ~70% to ~100%. Increasing the relative humidity (RH) in which *J*(V) was measured did not influence these values (across methyl (CH_3)-

or carboxyl (CO_2H)-terminated SAMs) over the range typically encountered in the laboratory (20-60% RH).

INTRODUCTION

Measurements of tunneling currents across insulating self-assembled monolayers (SAMs) are revealing the relationships between atomic/molecular-level structures of organic matter and this prototypically quantum behavior. The use of eutectic gallium indium alloy (EGaIn) electrodes in large-area (~100 μm^2) junctions[1-9] of the form Ag^{TS}/SAM//Ga_2O_3/EGaIn is a particularly convenient technique to use for physical-organic studies of charge transport across SAMs.[1-15] The role of gallium oxide (Ga_2O_3)—a film that forms spontaneously on the surface of the EGaIn[1,16,17]— is technically important in this type of junction, and must be understood in order to interpret results obtained using it; this oxide film might, in principle, influence the electrical characteristics of the top interface (the interface between the SAM, the Ga_2O_3 film, and the EGaIn), the mechanical stability of the junctions, and/or the sources of the dispersion (or spread, as measured by standard deviation) in the data. A number of factors might contribute to these characteristics, including the gaseous environment (i.e., the concentrations of O_2, H_2O, and other volatile components in the atmosphere) in which the EGaIn-based top electrode is formed, and the gaseous environment in which it is used. The history of use of the electrode, and the roughness (and thus the area of physical contact of the surface of the oxide with the SAM), are also important.

The objectives of this work were to determine i) the influence of the atmosphere in which Ga_2O_3/EGaIn "conical-tip" and "spherical hanging-drop" electrodes were formed and used on their electrical properties; ii) the influence of the Ga_2O_3 film (both when present, and when minimal or absent) on the absolute value, and standard deviation, of measurements of current density J at voltage V (J(V), A·cm^{-2}); and iii) the influence of the roughness of the Ga_2O_3 film on measurements on J(V).

The gallium oxide film, and the interface between this film and the SAM, are technically the most complicated components of the Ag^{TS}/SAM//Ga_2O_3/EGaIn junction. The Ga_2O_3 film—a thin (nominally ~0.7 nm[16]) film that forms on the surface of EGaIn upon exposure to air or O_2—is crucial to the characteristics and performance of the Ga_2O_3/EGaIn junction; it facilitates the formation of electrode tips with useful shapes and sizes. (In particular, it is the basis for the mechanical stability of what we call "conical tips"[6,17]). It allows the formation of tips with small radii of curvature (~25 µm). It permits measurements across small areas of contact (~100 µm^2 nominal area) as determined by optical microscopy—values substantially less than that in terms of the area of electrical contact involved in tunneling.

Measurements of charge transport across SAMs made over the course of several years using EGaIn-based junctions in ambient atmospheric conditions have suggested that the adsorption of adventitious materials from the atmosphere on the Ga_2O_3 film is normally not an important influence on the measured current density, or on the yield of working junctions (i.e. the ratio of non-shorting junctions to all measured junctions). For example, measurements of current density (J(V), A/cm^2 – J at applied bias V) are consistent and reproducible across samples and users; the distribution of data (log standard deviation, σ_{log}) ranges from ~0.2 to ~0.5 (from experiments replicated by multiple user)[18] for *n*-alkanethiolates on Ag^{TS} or Au^{TS} and ~0.1 – 0.2 for *n*-alkanecarboxylates[3] on Ag^{TS} (probably supported on a thin AgO_X surface film) in air (a value of σ_{log} ~0.3 corresponds to a range from ×0.5 to ×2.0 of the mean).

Formation of the conical tips, however, result in a rough (at the nanometer to micrometer scale), if flexible and compliant, Ga_2O_3 film. Although the Ga_2O_3 film is sufficiently electrically conductive that its resistance does not contribute significantly to, or interfere with, tunneling currents measured across SAMs,[16] its roughness leads to areas of electrical contact between the top Ga_2O_3/EGaIn electrode and the SAM-bound bottom electrode that are ~10^{-4} the geometrical contact area (as measured by optical microscopy).[1,19] We estimate that this value of 10^{-4} partitions into two components, a 10^{-3} contribution from the roughness of Ga_2O_3 and 10^{-1} from the roughness of the silver substrate.[1,20,21]

We designed a gas-tight chamber to control the atmospheric environment (i.e. the identity and concentration of the gas(es) comprising the atmosphere) in which we formed the Ga_2O_3/EGaIn electrodes, and (separately) in which we measured rates of charge transport across the molecular junction (Figure 1). The design of the chamber made it possible to change the composition of the atmosphere before and during formation of the tip and the junction, and independently, during measurements of J(V). The Supporting Information details the design and operation of the chamber.

We measured rates of charge transport through junctions incorporating two different substrates i) a SAM formed from *n*-dodecanethiol (SC_{12}) or 12-mercaptododecanoic acid ($SC_{11}CO_2H$) on template-stripped silver (Ag^{TS})[22]; the resulting junctions have the form Ag^{TS}-$S(CH_2)_{11}T$//Ga_2O_3/EGaIn, where T = CH_3 or CO_2H, and ii) a freshly cleaved, bare, graphite substrate[23,24] formed by gluing a highly-ordered pyrolytic graphite chip to a metal shim (to form a junction we describe as HOPG//Ga_2O_3/EGaIn). We also tested two different Ga_2O_3/EGaIn top-electrode geometries—a conical tip and spherical hanging-drop (Figure 1B). The contact surface of the conical-tip electrode is rough due to asperities in the oxide, these surface irregularities result during the formation of the tip (in particular, when the neck of the EGaIn breaks at the point of rupture).[1,16,19] Fabrication of the hanging-drop electrode, by contrast, does not require the EGaIn to rupture (Figure 1), and the surface of the electrode is therefore qualitatively smoother than that of a conical tip, and has (we believe) a thinner and more flexible Ga_2O_3 film. We measured junctions using both top electrode geometries in seven different environments: dry air (from a cylinder of compressed air), humid air (5-80% relative humidity (RH)), argon, nitrogen, oxygen, anhydrous ammonia, or air containing acetic acid. By forming the electrode in gases that have low concentrations of oxygen, we were able to limit or eliminate the formation of the oxide film on the EGaIn electrode.

This work led to four main conclusions. i) The gallium oxide on the surface of EGaIn contributes to the mechanical stability of the electrode, and is important for reproducible measurements of current density, $J(V)$, with narrow dispersions in data, σ_{log}. ii) The oxide film does not contribute significantly to the resistance of the junction. iii) Measurements of $J(V)$ using Ga_2O_3/EGaIn electrodes are not affected by changes in relative humidity over a range normally encountered in the laboratory. Junctions incorporating carboxyl terminated SAMs gave current densities at 5% RH that were approximately ×10 lower than at higher RH levels. iv) Junctions using hanging drop electrodes result in higher values of $J(V)$ than junctions using conical tip electrodes by $\Delta\log|J|_{mean} \sim 2$ to 3. We attribute this difference in $J(V)$ to differences in surface roughness between the conical and spherical drop electrodes.

BACKGROUND

Ga_2O_3/EGaIn top-electrode in molecular junctions. We use the Ga_2O_3/EGaIn-based junctions primarily for *physical-organic studies*—that is, studies that correlate *trends* in the structure of the molecules composing the SAM with *trends* in current density $J(V)$ (rather than for studies that establish absolute values of *J*(V)), for three reasons: i) The Ga_2O_3/EGaIn electrode makes it possible to form junctions with highly ordered SAMs conveniently (without expensive equipment and delicate operation of instruments), rapidly, and with high yields (>90%). It also yields very reproducible data (as do EGaIn-based measurements using other systems, such as cross-bar and microfluidic devices).[19,25] ii) The ease of use of this electrode makes it straightforward to collect large numbers (500–1000) of data per day, and therefore to generate reliable statistical information about replicability and reproducibility. iii) It can take full advantage of the ability of organic synthesis to provide easy access to a range of molecular structures appropriate for the formation of SAMs, and for testing hypotheses about relationships between tunneling current densities and molecular structure.[1-3,5,26-28]

Although the focus of our work is on physical-organic studies, we emphasize that we consider the absolute reproducibility and replicability of studies with conical tips (both flattened[1] and unflattened[2-4]) to be good relative to other methods (typically, one standard deviation in a fit of a Gaussian curve to the data corresponds to a factor of two to three in the value of *J*(V), although this number depends on several factors, including the structure of the molecules making up the SAM, the geometry of the tip, and the roughness of the surface of the metal of the bottom electrode).

Electrical properties of Ga_2O_3/EGaIn. Under ambient conditions, a thin self-limiting layer of Ga_2O_3 forms very rapidly[16] on the surface of bulk EGaIn.[17] When using EGaIn as a "soft" electrode, the resistivity of the oxide film might, in principle, influence measurements of electrical current or potential. We previously estimated the resistance of the Ga_2O_3 layer on EGaIn[1] by measuring the resistance of Ga_2O_3/EGaIn electrodes on a HOPG substrate forming a junction with the structure HOPG//Ga_2O_3/EGaIn. We inferred an ohmic mechanism of resistance, because log|*J*(V)| increased linearly with increasing voltage: the resistance of the oxide calculated for the Ga_2O_3 film was $R_{Ga2O3} = 3.3\times10^{-4}\ \Omega\cdot cm^{-2}$. This resistance is lower (by a factor of 10) than the resistance of a SAM composed of the shortest alkanethiolate (SCH_3, SC_1) ($R_{SC1} = 1.0\times10^{-3}\ \Omega\cdot cm^{-2}$).

The electrical[29-31] and physical properties of gallium oxide, and its reactivity towards different chemicals,[32-34] depends strongly on the method by which it is formed (the Supporting Information discusses the chemical reactivity of gallium oxide briefly). Gallium oxide, formed spontaneously on the surface of the EGaIn electrode, is probably much less structured and more conducting than pure gallium oxide (formed by vapor deposition at high temperatures[29], thermal annealing[30], or by epitaxial growth on GaAs[31]).

Simeone *et al.*[1] have compared a liquid drop of Hg and a conical tip Ga_2O_3/EGaIn electrode in measurements of a Fe/FeO_X susbtrate; where the FeO_X was the most resistive component of the junction. He created electrodes with equivalent nominal contact areas, and found the current density of the conical tip electrode was ~10^{-3} the value measured from the Hg-drop electrode. They concluded that the difference in current density was due to the fact that the Ga_2O_3/EGaIn conical-tip electrodes had a lower effective electrical contact area (probably due to the roughness of the electrode) than did the liquid Hg drop electrode.

Reactivity of Ga_2O_3 with water. Metal oxides have a higher surface free energy than hydrophobic *n*-alkanethiolate-based SAMs, and a partial monolayer of water forms on their surface at 10% relative humidity (RH) and a complete monolayer of water is believed to be present at 20% RH.[35] At higher levels of RH, multilayers of water form on the metal oxide substrate.[36] It is uncertain if this presumptive film of water persists (or in what form it persists) when the electrode is in contact with a hydrophobic SAM. For a SAM with a hydrophobic surface (here we use SAMs of *n*-dodecanethiolate on Ag^{TS}), spontaneous de-wetting is plausible at the interface between the SAM and the asperities on the surface of the Ga_2O_3. We also do not know the interfacial pressure of these asperities in contact with the SAM; this pressure might be sufficient to exclude water. It is also possible that local heating at the interface between the Ga_2O_3 and the SAM due to tunneling current (plausibly 10^2 A/cm^2)[37] might dry the contact regions.

We note and emphasize that the unknown influence of water on the electrical properties of a junction is not an uncertainty that is unique to EGaIn-based junction; this problem is relevant to *all* tunneling junctions that make measurements in ambient conditions.

EXPERIMENTAL

SAMs of Alkanethiolates. We used Ag^{TS} substrates bearing SAMs of *n*-dodecanethiolate (SC_{12}) as the standard (or reference) for comparison; measurements of current density across this SAM are well-characterized and replicable across many users.[1,3] We also used SAMs bearing a hydrophilic, polar terminal carboxylic acid ($SC_{11}COOH$) on Ag^{TS}: this SAM, which has a higher affinity for water molecules than does SC_{12},[38] allowed us to study the effect of environmental humidity on measurements of J(V).

Graphite substrate for examining atmospheric effects. We chose graphite (SP^3 HOPG, SPI Inc.) as a bottom electrode in some of our studies to provide a flat, well-defined surface that was unreactive toward the Ga_2O_3/EGaIn top electrode, unreactive toward O_2, and hydrophobic.[39,40] By using a freshly formed HOPG surface—generated by mechanical cleavage of the top layers of a piece of graphite glued to a metal shim—we could create a clean, flat, electrically conducting surface (r.m.s. roughness of 0.3-0.5 nm according to SPI technical specifications). By using graphite electrodes, we were able to attribute the majority of the variations observed as a result of changes in the environment to the Ga_2O_3 film, rather than to some other part of the junction.

Geometries of the EGaIn Electrode. We used two different Ga_2O_3/EGaIn electrode geometries: "selected" conical tips (Figure 1C), and spherical hanging-drops (Figure 1D). The conical tip is formed by bringing an extruded drop of EGaIn into contact with the silver substrate surface, and then pulled away from the surface until the neck ruptures into two parts (or "cones").[6,17] "Selected" conical tips (which we used here, show no visible asperities during formation) are distinct from "as-formed" conical tips. A conical tip formed during the rupture of the neck may have surface asperities which reflect the processes occurring during formation. One can reduce these asperities by pre-flattening the electrode on a flat surface— compressing any "as-formed" asperities—prior to use in a junction. A description of the "pre-flattened" tip method is found in the Supplemental Information.

"Selected" Conical Tips. Conical tips are easy to make, and enable the rapid fabrication of junctions that have a smaller nominal contact area (50 to 1000 μm^2) than those generated using the larger hanging-drop electrode. In our experience, junctions formed from conical-tip electrodes are less likely to short (~90% yield of working junctions) than hanging-drop electrodes of EGaIn (~30-60% yield). We assume that a large contact area and sensitivity to perturbation by mechanical vibration contributes to the lower yields of working junctions for the hanging-drop electrode, but have not studied the origins of these differences.

Visible asperities (i.e. whiskers) form on the surface of conical tips during the rupture of the neck (Figure 1B); these asperities are not reproducible, and contribute to dispersions in J(V) data. On average, the creation of a visible tip asperity occurs in approximately four of every ten tips formed. In order to avoid the ambiguities associated with such asperities, we examined the tip with a microscope after formation, and selected for use the conical tips that are free of visible surface irregularities. If a conical tip electrode forms visible asperities, it is discarded either by physical removal of the tip and extrusion of a fresh drop of EGaIn, or by reconnecting the tip with the EGaIn on the substrate and withdrawing the EGaIn into a new tip. This selection of conical-tip electrodes facilitates the collection of data with a narrow distribution (σ_{log}).

"Hanging-Drop" Electrode. Hanging-drop electrodes of EGaIn were used in certain experiments on both graphite and on SAMs as substrates. Hanging-drop electrodes allowed us to i) compare rates of charge transport across junctions with and without the gallium oxide film, ii) correlate data from different environments, including those where a conical tip cannot be formed or is not stable, and iii) reduce the uncertainty in the contact area of the junction resulting from any effects of atmosphere. Figure S1 shows SEM images suggesting the surface roughness associated with conical tips and spherical drops of Ga_2O_3/EGaIn.

Environmental Conditions. We used dry air from a compressed source (AI UZ300, Airgas Inc.) and generated low-oxygen atmospheres (<0.02% O_2 – our limit of detection) using Ar (99.999% purity, #AR UHP300, Airgas Inc.) or N_2 (99.999% purity, #NI UHP300, Airgas Inc.). For experiments in low-O_2 atmospheres, we began electrical measurements across the junction once the O_2 sensor (R-17D, Teledyne Analytical Instruments) indicated an O_2 concentration value of <0.2% (the minimum detectable reading for the instrument). We generated reactive atmospheres using O_2 and NH_3 gases (O_2 #OX300 and anhydrous NH_3 #AM AH35, Airgas). The acetic acid environment was generated by evaporation of glacial acetic acid (17.4 M, Sigma Aldrich) into a flowing stream of air. We did not control the concentration of the acetic acid in the vapor phase.

RESULTS AND DISCUSSION

Performance of EGaIn Junctions in Alternate Environments on Graphite Substrates. For measurements on graphite (no SAM present) bottom electrodes, the environmental chamber was conditioned first with the target atmosphere, followed immediately by extrusion of an EGaIn drop (conical-tip electrodes were first formed in air before environmental conditioning of the chamber) or formation of a conical tip electrode). The EGaIn electrode, thus fabricated, was lowered onto the graphite substrate to form an electrical junction.

Figure 2 displays histograms of log|*J*(-0.5 V)| collected using hanging-drop electrodes on graphite substrates; Table 1 summarizes these measurements. We did not observe a significant difference in the electrical characteristics of the EGaIn drop electrode when we changed the environment (between dry air, O_2, Ar, and N_2) in which it was formed and the junction was measured (Figure 2A-D); in particular, the mean values and standard deviations of log|*J*| (in units of A/cm^2) are indistinguishable (log|*J*| = 4.4, $\sigma_{\log} = 0.25$). EGaIn drops formed in air and O_2 have surface films of Ga_2O_3, while those formed in N_2 or Ar either do not, or have only a thin or partial film: We therefore conclude that the Ga_2O_3 film does not contribute to the resistance of the junction and also does not influence the effective electrical contact area. This conclusion reinforces similar conclusions reached in previous but different studies.[1,16]

Hanging Drop Electrodes Formed in Air or O_2 and Measured in Air or O_2. Figure 2 A and B summarizes measurements using hanging-drop electrodes formed in O_2-containing atmospheres (air and O_2, respectively) and a HOPG substrate; we assume that the surface of these drop electrodes have a Ga_2O_3 film that is chemically similar to that formed on conical tip electrodes (although not as severely buckled and probably—because it is less buckled and folded—substantially thinner and more compliant). Forming the electrode in a high-O_2 atmosphere (> 99.8%) rather than air does not influence the resistance of the oxide film, or that of the junction formed with a graphite substrate. Thus, the resistance of the oxide is not sensitive to small changes in the O_2 concentration in which it is formed, and—as observed previously—is too small to influence the tunneling currents measured though SAMs.

Junctions using a conical tip electrode on a HOPG substrate were measured in selected atmospheres of air, argon, and anhydrous ammonia. Figure S5 of the SI summarizes these data. As we observed with measurements using a drop electrode, there was no significant difference between measurements obtained with electrodes *formed* in air, and *measured* in air or argon. We conclude that the presence of O_2 in the atmosphere during measurements of J(V) does not play a role in the resistance of the junction. The surface roughness of the conical tip electrodes correlated with a decrease of the measured current density: the difference between the smoother hanging-drop electrodes and the rougher conical tip electrodes was $\log|J|_{\mathrm{mean}}$ ~1.3.

Hanging Drop Electrodes Formed in Ar or N_2 and Measured in Ar or N_2. Atmospheres of N_2 (Figure 2C) or Ar (Figure 2D) contained O_2 concentrations at less than 0.2%. We believe that the low-O_2 environments resulted in EGaIn drops that certainly did not have the same Ga_2O_3 film that normally forms on the surface of EGaIn in air, and may only have a partial, or incomplete, thin film. Junctions formed with these electrodes on a graphite substrate had values of $\log|J|_{\mathrm{mean}}$ similar to those formed under air and pure O_2. This result confirms that the presence or absence of the oxide on the electrode surface has no influence on the mean value of J(V).

This observation is consistent with previous inferences;[1,16] the oxide film seems to serve primarily as a solid, conducting layer that resists compression, that bends easily, and that fractures on extension. This layer allows the formation of stable junctions in high yield, but does not contribute significantly to the electrical resistance of the junction.[1]

Hanging Drop Electrodes Formed in "Reactive" Vapor and Measured in "Reactive" Vapor. When drops were formed in an atmosphere of anhydrous ammonia (Figure 2E), the value of log|*J*|$_{mean}$ seems to be slightly lower than junctions formed under air, O_2, N_2, or Ar, but the distribution was broader than those junctions, and the statistical significance of the difference was low. Ammonia vapor thus appears to be similar to N_2 or Ar as an "inert atmosphere," but with some other currently undefined surface chemistry contributing to a broader dispersion in values of *J*(V).

Measurements in air containing high concentrations of acetic acid (AcOH) vapor appeared to be bimodal (Figure 2F). We speculate that the low values of log|*J*|$_{mean}$ observed reflect a surface covered with a film of a gallium or indium acetate (or a multilayer soap) but we have no evidence that directly supports this conjecture.

The Influence of Gaseous Environments on the Electrical Characteristics of $Ag^{TS}S(CH_2)_{11}CH_3//Ga_2O_3/EGaIn$ Junctions. We measured charge tunneling across junctions using hanging drop electrodes and "selected" conical tips showing no visible asperities.

Formation of "Selected" Unflattened Conical Tip Electrodes. We first conditioned the environmental chamber with air (from a compressed source) and subsequently formed conical tip electrodes (Figure 1B). After formation of the tip, the gas feed to the chamber was either left unchanged, or changed to another atmosphere, and the electrical characteristics of the junctions were measured. When a junction shorted, we purged the chamber with air and formed a new tip, and again purged the chamber with the atmosphere to be examined.

We were unable to form conical tip electrodes under either Ar or N_2 (Table 1) because, in the absence of O_2, the structurally stabilizing oxide film does not form. When attempting to form the conical tip by retracting the drop following contact with the substrate, the drop detached from the syringe rather than stretching and breaking. Histograms of log|*J*(-0.5V)| collected from junctions of conical Ga_2O_3/EGaIn tips formed in air and then used in measuring current densities across a $Ag^{TS}SC_{12}$/Ga_2O_3/EGaIn junction in air, O_2, Ar, and N_2 showed no significant difference (Figure 3).

Conical Tip Electrodes Formed in Air and Measured in Ar, N_2, NH_3,and HOAc/Air. Measurements obtained under a N_2 atmosphere (Figure 3C) provided $\log|J|_{mean}$ values similar to those measured in air. The majority of measurements in Ar (Figure 3D) are also similar, although they include several outlying points near log|*J*| ~ 0.5 (these points are not included in the Gaussian fitting) and a few at log |*J*| = +4.2; the latter are shorted junctions.

The cluster of data at log|*J*| ~0.5 may be a result of junctions in which the Ga_2O_3 film ruptured (Figure S1C shows such ruptures) while the tip was in contact with the SAM; in this circumstance, because the concentration of O_2 is low, the gallium oxide film would not reform. The resulting junction, post rupture, would plausibly have a greater area of effective electrical contact than junctions formed with typically rough conical tips, and thus give a mean value of log|*J*(V)| approximately two to three times greater than typical conical tips. This increase in contact area is observed when comparing the log|*J*| values of conical tip and drop junctions measured on SAM substrates. In air, $\log|J|^{drop} - \log|J|^{conical} \approx 1.8$, while in a nitrogen environment the difference is ~2.8. These values are in rough agreement with those reported by Simone *et al.*[1] where the conformal nature of a Hg drop caused an observed increases of ~10^3 in *J*(V) relative to the contact area of a conical tip junction.

Interestingly, junctions measured in the ammonia atmosphere gave values with $\log|J|_{mean}$ = +0.4 (Figure 3E)—an increase of approximately three orders of magnitude relative to values in air, O_2 and N_2 (Figure 3 A,B,C) and approximately the same as the cluster of values observed under Ar (Figure 3D). We did not observe electrical shorts in the ammonia atmosphere. To eliminate the possibility of damage to the SAM from exposure to ammonia, we changed the atmosphere from ammonia vapor to air (with the same EGaIn tip electrode and without changing the substrate) and the measured current density returned to that expected in air (Figure S6). We conclude, therefore, that the ammonia does not damage the SAM. There seem to be at least two possible rationalizations for the behavior in NH_3, both of which would increase J(V) by increasing the effective electrical contact area (relative to measurements in air): i) In one, the ammonia would provide (perhaps by corrosion of the Ga_2O_3) a thinner and more easily deformable (and hence more compliant) oxide film than the one formed in air: ii) In a second, the ammonia would act as an "inert gas", similar to Ar, and prevent the growth of an oxide film in regions where the film is cracked. Why all of the measurements in ammonia would present this behavior, and only a few in Ar, is not evident from the available data, although adsorption of NH_3 on the surface of the EGaIn is a plausible possibility.

The data obtained using a conical tip formed in air and measured in a HOAc/air atmosphere were too scattered to provide a useful interpretation beyond the fact that the acetic acid seems to be reactive toward the Ga_2O_3 and/or the SAM.

Junction Measurements Using Hanging Drop Electrodes. We also formed junctions using hanging drop EGaIn electrodes on *n*-dodecanethiolate (SC_{12}) modified Ag^{TS} substrates (Figure 4). The drops were first formed in air—thus ensuring they had a Ga_2O_3 film on their surface. Measurements in air resulted in $\log|J| = -0.6$, compared to -2.4 for conical tips in the same atmosphere. We attribute this increase in current density ($\Delta\log|J| \sim 1.8$; $|J|^{drop}/|J|^{conical} \sim 100$) to an increase in electrical contact area; hanging-drop electrodes have a lower surface roughness and therefore better conformal contact with the substrate than conical tips. In measurements taken in low-O_2 atmospheres (Ar and N_2), we observed an additional increase in current density to log|J| = +0.3 with drop electrodes resulting in Δlog|J| ~2.8 ($|J|^{\mathrm{drop}}/|J|^{\mathrm{conical}}$ ~1000). This increase, again, is probably due to the rupture of the oxide film on the drop electrode, resulting in junctions having no Ga_2O_3 film at the top interface between SAM and top-electrode.

When we formed *and measured* the hanging-drop electrode in N_2, the yield of working junctions was 7%: all but one junction formed with the SAM resulted in an electrical short at some inconsistent point during measurements (consisting of 20 J-V scans), the J-V characteristics of the trace demonstrated an electrical short. Portions of the traces were measured at log |J| = +0.3, suggesting the creation of an oxide-free junction prior to the failure of the junction.

Figure 5 summarizes all junctions (comprising conical and drop electrodes and SAMs of *n*-dodecanethiolate) that resulted in data appropriate for a Gaussian fitting, including outliers. Although junctions formed using conical-tip and drop electrodes have different current densities when measured under air (or oxygen containing atmospheres), both top-electrode geometries result in similar performance in low-oxygen environments. This observation suggests that, in low-oxygen environments, differences in roughness of these two types of electrode do not make the two measurements of current density distinguishably different. We speculate that in low-oxygen atmospheres, ruptures on the electrode may result in regions of contact between eutectic metal and the SAM, instead of the Ga_2O_3 film; the liquid metal would have a different wetting or conformal contact with the SAM, resulting in an increase in the measured current density for the junction due to an increase in the effective electrical contact area.

Effect of Relative Humidity on Measurement of *J*(V). We examined the effect of relative humidity on both graphite and SAM-based junctions. We used the conical-tip electrode to contact the SAM, and a hanging-drop electrode to contact the graphite. Figure 6 indicates that

J(V) is insensitive to humidity on both the graphite substrate (HOPG//Ga_2O_3/EGaIn, square) and the SAM (Ag^{TS}-$S(CH_2)_{11}CH_3$//Ga_2O_3/EGaIn, circle). Junctions having a carboxylic acid-terminated SAM (triangle) were not sensitive to changes in humidity (over a range typically encountered in the laboratory, (20-60 RH%). In a separate study,[41] measurements of $SC_{11}CO_2H$ SAMs in ambient conditions gave *J*(V) = -2.1 (~ 35% RH) while $SC_{11}CH_3$ SAMs gave *J*(V) = -1.3 (~45% RH), both giving $\sigma_{log} = 0.4$; these values are consistent with our measurements (within one standard deviation of the error) and demonstrate that SAMs of $SC_{11}CO_2H$ gives *J*(V) values lower than those of $SC_{11}CH_3$. We observe, however, that for carboxyl-terminated SAMs at 5% RH, where we expect the system to be dry, there is a decrease in the *J*(V) measured. We speculate that some water condensation in the junction at higher values of RH provides either i) a slight decrease in the height of the tunneling barrier (relative to air), or ii) a slight increase in the area of effective electrical contact (depicted in Figure S7).

CONCLUSIONS

We had two objectives in this work. i) To investigate the influence of different environmental conditions (i.e., different gases surrounding the Ga_2O_3/EGaIn tip and the junctions at room temperature) on fabrication of the tip, and on the measured current densities, *J*(V), across the tunneling junctions. ii) To study the influence of the surface roughness associated with the Ga_2O_3 on measurements of *J*(V) by comparing results obtained with the rougher conical tip and the smoother, although less stable, hanging drop. We summarize our findings in four points.

The Ga_2O_3 film does *not* contribute to the resistivity of the junction. Junction measurement on graphite using hanging-drop electrodes formed under N_2 or Ar (presumably with little or no oxide film) demonstrated current densities similar to measurements made with hanging-drop electrodes formed in the presence of O_2, possessing a film of Ga_2O_3 on the electrode surface (Figure 2). Measurements on SAMs using conical-tip electrodes (Figure 3) also demonstrated current densities similar to those in junctions formed either in low-oxygen (Ar, N_2) or O_2-containing (air, O_2) atmospheres. For these measurements, the conical tips were first formed in air (ensuring a Ga_2O_3 film on the electrode), and then measured in different atmospheres. Measurements in an ammonia atmosphere were the only ones giving J(V) values different from measurements in air, possibly due to adsorption of ammonia to the oxide film, or some other interaction with the gas.

The use of electrodes with thicker or thinner Ga_2O_3 films thus does not seem to influence the resistance of the top electrode and has no observable effect on J(V) measurements. This conclusion is consistent with our previous conclusions that the resistance of the Ga_2O_3 film is at least an order of magnitude smaller than the shortest alkyl SAM (methylthiolate), and consequently does not contribute significantly to the overall resistance of the tunneling junction.[1,16]

The Ga_2O_3 film on the EGaIn electrode influences junction stability. The presence of the Ga_2O_3 film increases the yields of working electrodes (>70%) and the reproducibility of the area of electrical contact with the bottom substrate, and thus contributes to the generation of reproducible values of J(V),with standard deviations of σ_{log}~0.3. Junctions consisting of conical tip and hanging-drop electrodes created in air, and measured in O_2-containing atmospheres, had working yields of 100%. For junctions measured in low-oxygen atmospheres, the working yield decreased to a range between 60-85%. This decrease suggests that the presence of oxygen, contributes to improved electrode performance and to reproducibility in J(V) measurements by reforming the oxide film on the EGaIn electrodes. Under low-oxygen environments, measurements of *J*(V) had larger standard deviations, perhaps due to cracking of the oxide film and idiosyncratic increases in the contact of the SAM with liquid EGaIn.

At the beginning of our studies of tunneling across SAMs using "EGaIn" electrodes, we used a conical shaped Ga_2O_3/EGaIn, but did not understand the characteristics of this electrode in any detail. Uncertainties included the importance of the roughness of the oxide film, the variability in the area of electrical contact of the EGaIn film with the surface of the SAM, and the influence of the surface chemistry of the EGaIn film on the performance of the top electrode. This work, in combination with other studies,[1,16] enables us to resolve problems associated with the characteristics of EGaIn electrode, and the contribution to the stability and reproducibility of tunneling junctions.

There is no statistically distinguishable effect of normal humidity fluctuations on measurements of current density using EGaIn-based junctions. Current density measurements on graphite, methyl-, and carboxyl-terminated SAM substrates are not significantly influenced by changes in the relative humidity (RH) within a range typically encountered in the laboratory (20-60% RH). When the atmosphere is dry (RH <5%), measurements of current density decreased across carboxyl-terminated SAMs but not across methyl-terminated SAMs. This observed decrease in current density may reflect a change in the interface of the very hydrophobic carboxyl-terminated SAM with the Ga_2O_3 film (Figure S7). At low humidity there is no or little water layer(s) adsorbed on the surfaces of the Ga_2O_3 and the CO_2H-terminated SAM. The surface free energy of the CO_2H-terminated SAMs (unlike that of methyl-terminated SAMs) may induce formation of a water layer onto its surface at higher values of RH.

Surface roughness in the EGaIn electrode influences *J*(V). Because the rupture of the EGaIn neck during formation of the conical tip is not entirely replicable, the surface film of Ga_2O_3 of conical tips has a significant, but unquantified roughness (Figure S1 A and B). Formation of the drop electrode, on the other hand, does not require this rupture, and is therefore smoother (Figure S1 C).

The oxide film on the hanging drop electrode seems more flexible and thinner than that formed on the conical electrode. These characteristics (or others) results in higher values of *J*(V) than those obtained with a conical tip the same SAM: measurements across a C_{12} SAM in air give $\log|J|_{\text{mean}} = -2.4$ for a conical tip and $\log|J|_{\text{mean}} = -0.6$ for a drop electrode; $\Delta\log|J|\sim1.8$ (e.g., $|J|^{\text{drop}}/|J|^{\text{conical}} \sim100$). The only difference that we have identified between these two measurements is the roughness of the Ga_2O_3 film, and thus the electrode surface. When we compare measurements in the N_2 atmosphere, we observed that $\log|J|_{\text{mean}}$ for a drop electrode is higher by a factor of ~2.8 than $\log|J|_{\text{mean}}$ for a conical electrode ($|J|^{\text{drop}}/|J|^{\text{conical}}\sim1000$). We suggest that the thin, compliant oxide film on the hanging drop electrode leads to more conformal contact with the surface of the SAM. In these comparisons the only uncontrolled variable was the roughness of the oxide film, all variables were held constant to the best of our abilities.

These results parallel results from Simeone *et al.*,[1] where a conformal Hg drop electrode measured on an Fe_2O_3/Fe substrate gave $\sim10^3$ higher current density values than an EGaIn conical tip electrodes on the same substrate. In both cases, increases in electrode roughness lead to weaker electrical contact, and to a decrease in the measured current density. We note that our results do not take into account the influence of the roughness of the substrate, which might also influence the electrical contact area of the junction.

FIGURES

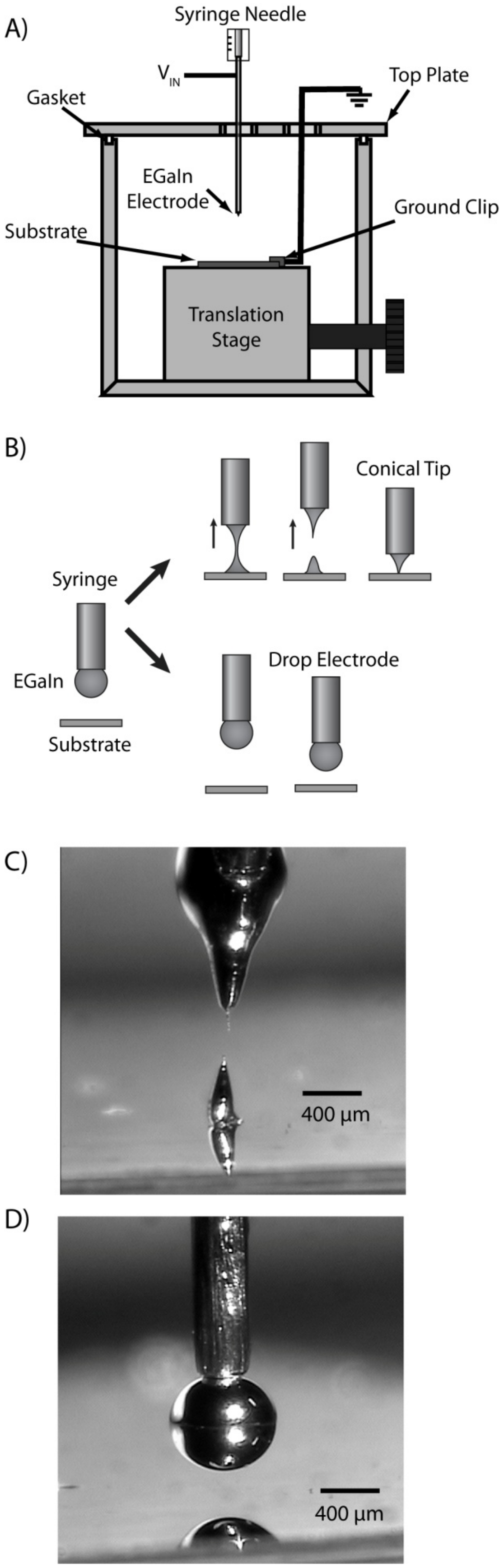
A)
Syringe Needle
V_IN
Top Plate
Gasket
EGaIn Electrode
Ground Clip
Substrate
Translation Stage
B)
Conical Tip
Syringe
EGaIn
Substrate
Drop Electrode
C)
400 µm
D)
400 µm

Figure 1. A cross sectional illustration of the environmental chamber (not to scale) (A), a schematic representation of methods to form either a conical-tip or hanging-drop Ga_2O_3/EGaIn electrodes from an extruded drop (B), microscopic images of a conical Ga_2O_3/EGaIn tip (C) and drop electrode (D). In some instances, during the formation of conical tips a whisker forms (C). These tips are often discarded, and a new tip is formed until the rupture does not create such an asperity. Further information about the operation of the chamber can be found in the Supporting Information.

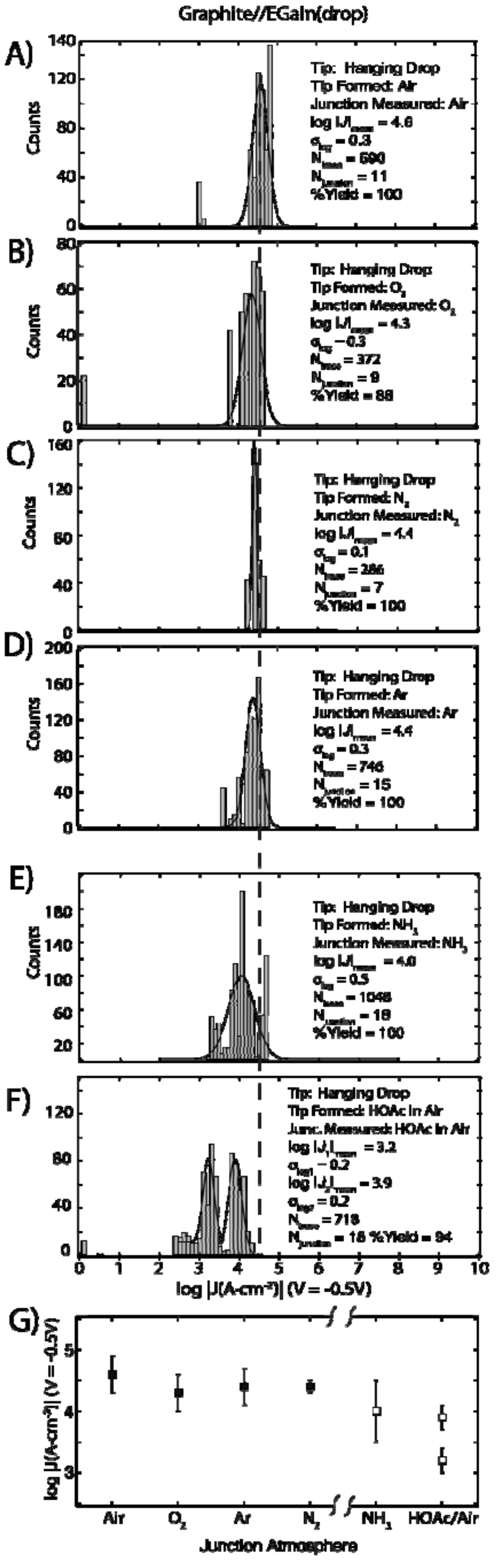
Graphite//EGaIn(drop)
A)
B)
C)
D)
E)
F)
G)
Counts
Tip: Hanging Drop
Tip Formed: Air
Junction Measured: Air
$\log |J|_{mean} = 4.6$
$\sigma_{log} = 0.3$
$N_{trace} = 590$
$N_{junction} = 11$
%Yield = 100
Tip: Hanging Drop
Tip Formed: O_2
Junction Measured: O_2
$\log |J|_{mean} = 4.3$
$\sigma_{log} = 0.3$
$N_{trace} = 372$
$N_{junction} = 9$
%Yield = 88
Tip: Hanging Drop
Tip Formed: N_2
Junction Measured: N_2
$\log |J|_{mean} = 4.4$
$\sigma_{log} = 0.1$
$N_{trace} = 286$
$N_{junction} = 7$
%Yield = 100
Tip: Hanging Drop
Tip Formed: Ar
Junction Measured: Ar
$\log |J|_{mean} = 4.4$
$\sigma_{log} = 0.3$
$N_{trace} = 746$
$N_{junction} = 15$
%Yield = 100
Tip: Hanging Drop
Tip Formed: NH_3
Junction Measured: NH_3
$\log |J|_{mean} = 4.0$
$\sigma_{log} = 0.5$
$N_{trace} = 1048$
$N_{junction} = 18$
%Yield = 100
Tip: Hanging Drop
Tip Formed: HOAc in Air
Junc. Measured: HOAc in Air
$\log |J_1|_{mean} = 3.2$
$\sigma_{log1} = 0.2$
$\log |J_2|_{mean} = 3.9$
$\sigma_{log2} = 0.2$
$N_{trace} = 718$
$N_{junction} = 18$ %Yield = 94
0 1 2 3 4 5 6 7 8 9 10
$\log |J(A\text{-}cm^{-2})|$ (V = -0.5V)
$\log |J(A\text{-}cm^{-2})|$ (V = -0.5V)
Air
O_2
Ar
N_2
NH_3
HOAc/Air
Junction Atmosphere

Figure 2. Histograms of the current density of EGaIn drop electrode junctions on a graphite substrate. Measurements were collected in an atmospheric chamber where we altered the composition of the environment in which the tips were formed and junctions were measured. "Tip Formed" represents the atmosphere in which the electrode was formed in; "Junction Measurement" refers to the atmosphere in which the junction is created (using the electrode formed in the "Tip Formed" atmosphere). The gases used were: A, compressed air; B, oxygen; C, nitrogen; D, argon; E, anhydrous ammonia; F,and acetic acid in air . Current density values ($\log|J(-0.5V)|$) are estimated from Gaussian fit to the histogram. Number of scans (N_{traces}), number of junctions ($N_{junctions}$) mean (for $\log|J|$), and standard deviation (σ_{log}) are presented for each atmosphere. A summary of data obtained by fitting Gaussian curves to histograms for each atmosphere is given in G.

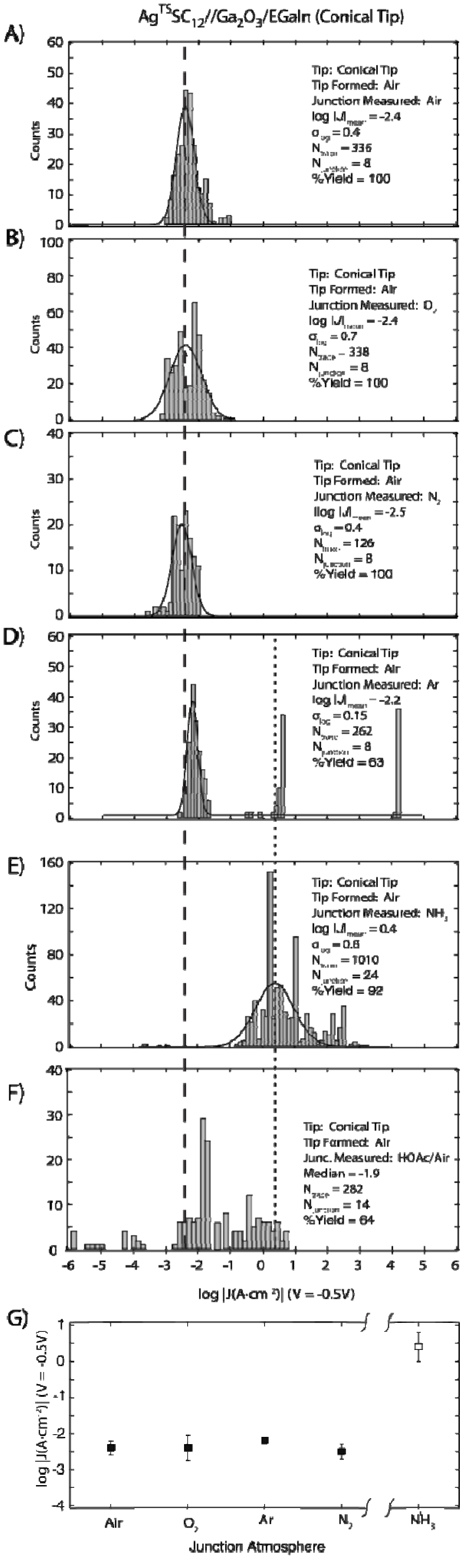
$Ag^{TS}SC_{12}//Ga_2O_3/EGaIn$ (Conical Tip)
A)
Tip: Conical Tip
Tip Formed: Air
Junction Measured: Air
log |J|$_{mean}$ = -2.4
σ_{log} = 0.4
N_{trace} = 336
$N_{junction}$ = 8
%Yield = 100
B)
Tip: Conical Tip
Tip Formed: Air
Junction Measured: O_2
log |J|$_{mean}$ = -2.4
σ_{log} = 0.7
N_{trace} = 338
$N_{junction}$ = 8
%Yield = 100
C)
Tip: Conical Tip
Tip Formed: Air
Junction Measured: N_2
log |J|$_{mean}$ = -2.5
σ_{log} = 0.4
N_{trace} = 126
$N_{junction}$ = 8
%Yield = 100
D)
Tip: Conical Tip
Tip Formed: Air
Junction Measured: Ar
log |J|$_{mean}$ = -2.2
σ_{log} = 0.15
N_{trace} = 262
$N_{junction}$ = 8
%Yield = 63
E)
Tip: Conical Tip
Tip Formed: Air
Junction Measured: NH_3
log |J|$_{mean}$ = 0.4
σ_{log} = 0.8
N_{trace} = 1010
$N_{junction}$ = 24
%Yield = 92
F)
Tip: Conical Tip
Tip Formed: Air
Junc. Measured: HOAc/Air
Median = -1.9
N_{trace} = 282
$N_{junction}$ = 14
%Yield = 64
Counts
-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6
log |J(A·cm^{-2})| (V = -0.5V)
G)
log |J(A·cm^{-2})| (V = -0.5V)
1 0 -1 -2 -3 -4
Air
O_2
Ar
N_2
NH_3
Junction Atmosphere

Figure 3. Histograms of current density measured with Ga_2O_3/EGaIn conical tip electrodes on a dodecanethiol SAM substrate forming junctions with the structure Ag^{TS}-$S(CH_2)_{11}CH_3$//Ga_2O_3/EGaIn. "Tip Formed" represents the atmosphere in which the electrode was formed in; "Junction Measurement" refers to the atmosphere in which the junction is created (using the electrode formed in the "Tip Formed" atmosphere). All tips were first formed in air, junction formation and measurements were collected within the target atmosphere Junctions were formed under: A, air; B, oxygen; C, nitrogen; D, argon; E, ammonia; F, acetic acid vapor in air. Current density values (log|*J*(-0.5V)|) are estimated from Gaussian fit to the histogram. Number of scans (N_{traces}), number of junctions ($N_{junctions}$), mean (for log|*J*|), and standard deviation (σ_{log}) are presented for each atmosphere. The Gaussian fit for argon (D) was measured for the first mode of the data at log(*J*) = -2.2. No Gaussian was fit to the acetic acid data (F). A summary of Gaussian fit data for each atmosphere is given in G.

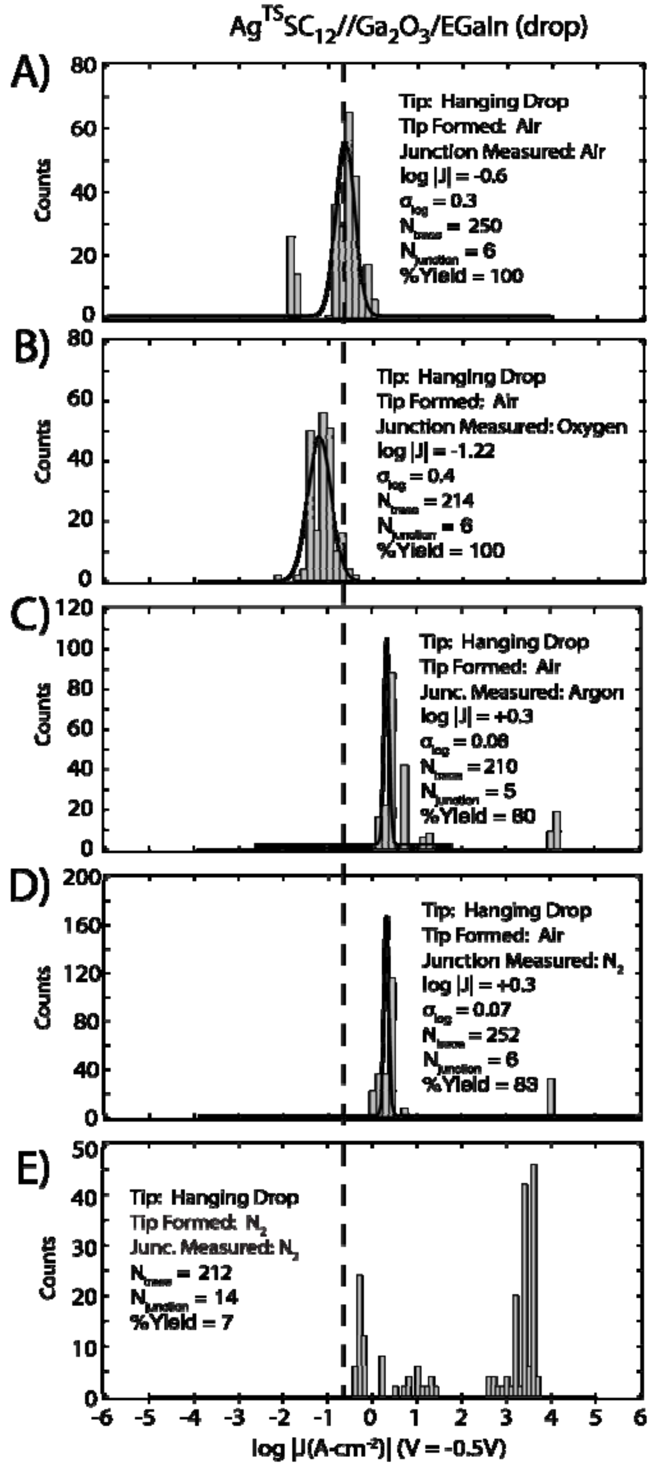

Figure 4. Histograms of current density measured with Ga_2O_3/EGaIn hanging-drop electrodes on a dodecanethiol SAM substrate forming junctions with the structure Ag^{TS}-$S(CH_2)_{11}CH_3$//Ga_2O_3/EGaIn. Junctions were formed under: A, air; B, oxygen; C, argon;

and D, nitrogen. Additionally E displays measurements from a drop electrode formed and measured under nitrogen; to prevent the formation of an oxide film on the drop. Current density values (log|*J*(-0.5V)|) are estimated from Gaussian fit to the histogram. Number of scans (N_{traces}), number of junctions ($N_{junctions}$), mean (for log|*J*|), and standard deviation (σ_{log}) are presented for each atmosphere.

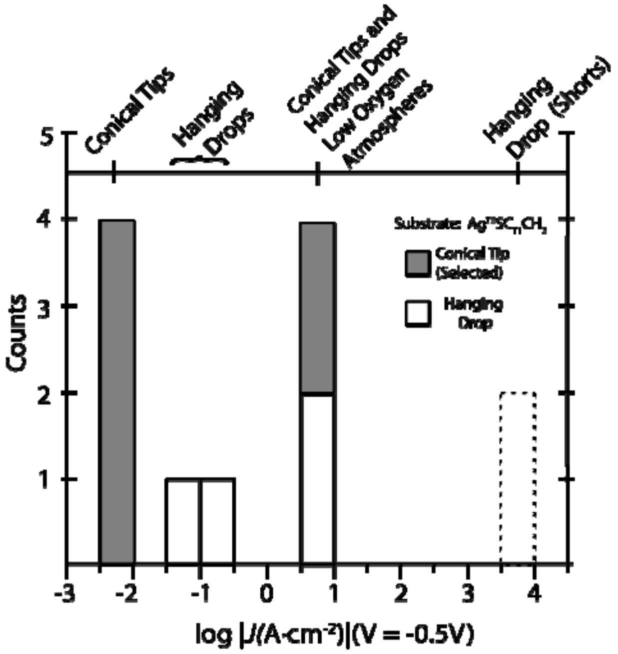

Figure 5. Collection of log|*J*|$_{mean}$ values for Ga_2O_3/EGaIn electrodes, both conical tip and hanging drop, forming junctions on a dodecanethiol SAM substrates in various atmospheres.

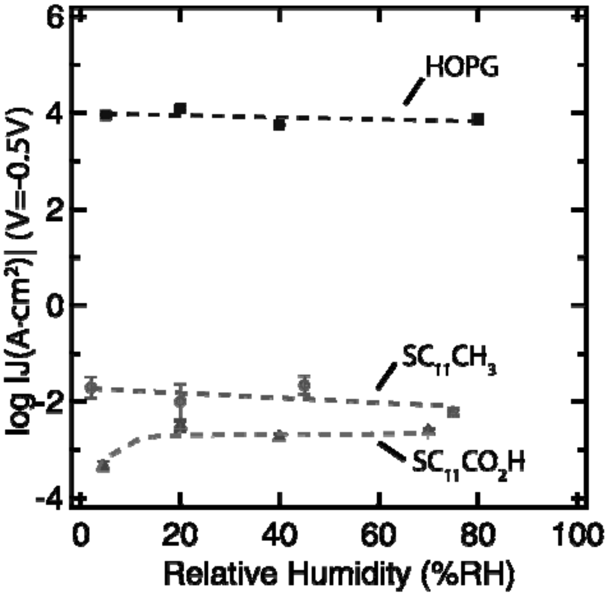

Figure 6. Plot of influence of humidity on the current density of conical tip Ga_2O_3/EGaIn electrodes on HOPG graphite (square), Ag^{TS}-$S(CH_2)_{11}CH_3$ (circle), and Ag^{TS}-$S(CH_2)_{11}COOH$ (triangle) substrates. Measurements were performed in a humidity-controlled atmospheric chamber. A hanging-drop electrode was used on the graphite substrate, a conical-tip electrode was used on the SAMs.

Table 1. Summary of tip formation and junction performance in various atmospheres

	Conical Tip (Selected)					Hanging Drop				
	Atmosphere of Tip Formation	Atmosphere of Junction Measurement	log $\lvert J(-0.5\mathrm{V})\rvert$ $(\mathrm{A/cm^2})\rvert$	$\sigma_{\log}$	Yield (%)	Atmosphere of Tip Formation	Atmosphere of Junction Measurement	log $\lvert J(-0.5\mathrm{V})\rvert$ $(\mathrm{A/cm^2})$	$\sigma_{\log}$	Yield (%)
SC_{12} SAM	Air	Air	-2.4	0.4	100	Air	Air	-0.6	0.3	100
	Air	O_2	-2.4	0.7	100	Air	O_2	-1.2	0.4	100
	Air	Ar	-2.2[a]	0.2[a]	60	Air	Ar	0.3	0.08[a]	80
	Air	N_2	-2.5	0.4	100	Air	N_2	0.3	0.07[a]	83
	Air	NH_3	0.4	0.8	85	Air	NH_3			
	Air	HOAc vapor	—	—	64	Air	HOAc vapor			
Graphite (HOPG)	Air	Air	3.3	0.2	100	Air	Air	4.6	0.3	100
	Air	O_2	3.1	0.1	100	O_2	O_2	4.3	0.3	88
	Air	Ar				Ar	Ar	4.4	0.3	100
	Air	N_2				N_2	N_2	4.4	0.1	100
	Air	NH_3				NH_3	NH_3	4.0	0.5	100
	Air	HOAc vapor				HOAc vapor	HOAc vapor	3.2, 3.9[b]	0.2	94

[a] Gaussian distribution calculated for data near the mean, excluding anomalous data

[b] The data seems to have a bimodal distribution

ASSOCIATED CONTENT

Supporting Information. Ga_2O_3 reactivity with acids; discussion of EGaIn tip preparation methods; atmospheric chamber design and operation; SAM preparation; Ga 3d, O 1s, and C 1s XPS data and analysis; SEM images of tips; image sequence of conical tip degredation in AcOH atmosphere; *J*(V) histogram of conical tips on graphite substrates in air, Ar, and NH_3; *J*(V) of single electrode exposed to air, NH_3, air again; schematic of humidity interacting with oxide surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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ABBREVIATIONS

EGaIn, eutectic gallium indium; SAM, self-assembled monolayer; Ag^{TS}, template-stripped silver; HOPG, highly ordered pyrolytic graphite; AcOH, acetic acid; RH, relative humidity; SEM, scanning electron microscope.

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