

Influence of Environment on the Measurement of Rates of Charge Transport across $\text{Ag}^{\text{TS}}/\text{SAM}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ Junctions

Jabulani R. Barber,[†] Hyo Jae Yoon,^{†,‡} Carleen M. Bowers,[†] Martin M. Thuo,[†] Benjamin Breiten,[†] Diana M. Gooding,[†] and George M. Whitesides^{*,†,§}

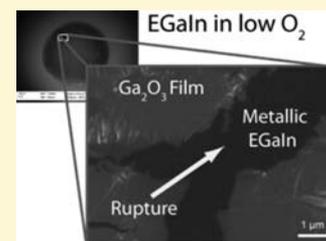
[†]Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, United States

[‡]Department of Chemistry, Korea University, 5 Anam-dong, Sungbuk-gu, Seoul 136-701, Republic of Korea

[§]Kavli Institute for Bionano Science & Technology, School of Engineering and Applied Sciences, Harvard University, Pierce Hall, 29, Oxford Street, Cambridge, Massachusetts 02138, United States

S Supporting Information

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) (the so-called “EGaIn” electrodes), and in measurements of current density, $J(V)$ (A/cm^2), across self-assembled monolayers (SAMs) incorporated into $\text{Ag}/\text{SR}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ 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, as well as air containing vapors of acetic acid or 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, micrometer-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 $\log |J|_{\text{mean}} = -2.4 \pm 0.4$ for the conical tip, and $\log |J|_{\text{mean}} = -0.6 \pm 0.3$ for the drop electrode (and, thus, $\Delta \log |J| \approx 1.8$); 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. However, the presence of an oxide film did improve the stability of junctions and increase the yield of working electrodes from $\sim 70\%$ to $\sim 100\%$. 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) reveal 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 ($\sim 100 \mu\text{m}^2$) junctions^{1–9} of the form $\text{Ag}^{\text{TS}}/\text{SAM}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ (where “/” refers to an ionic or covalent interface, and “//” indicates a van der Waals interface) 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)—which is a film that forms spontaneously on the surface of the EGaIn^{1,16,17}—is technically important in this type of junction, and it 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. Many 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 $\text{Ga}_2\text{O}_3/\text{EGaIn}$ “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)

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on the absolute value, and standard deviation, of measurements of current density J at voltage V ($J(V)$, given in units of $A\text{ cm}^{-2}$); 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 $\text{Ag}^{\text{TS}}/\text{SAM}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ junction. The Ga_2O_3 film—which is a thin (nominally $\sim 0.7\text{ nm}$)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 $\text{Ga}_2\text{O}_3/\text{EGaIn}$ 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 ($\sim 25\text{ }\mu\text{m}$), as measured by optical microscopy, and permits measurements across small areas of contact ($\sim 100\text{ }\mu\text{m}^2$ nominal area). The optically measured nominal contact area is believed to be substantially larger than 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 nonshorting junctions to all measured junctions). For example, measurements of current density ($J(V)$, $A/\text{cm}^2 - J$ at an 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 users)¹⁸ for n -alkanethiolates on Ag^{TS} or Au^{TS} and ~ 0.1 – 0.2 for n -alkanecarboxylates³ on Ag^{TS} (probably supported on a thin AgO_x surface film) in air (a value of $\sigma_{\log} \sim 0.3$ corresponds to a range from $0.5\times$ to $2.0\times$ of the mean).

Formation of the conical tips, however, results in a rough (at the nanometer to micrometer scale), if not flexible and compliant, Ga_2O_3 film. Although the Ga_2O_3 film is sufficiently electrically conductive, so 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 $\text{Ga}_2\text{O}_3/\text{EGaIn}$ electrode and the SAM-bound bottom electrode that are $\sim 10^{-4}$ 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 $\text{Ga}_2\text{O}_3/\text{EGaIn}$ 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 ($\text{SC}_{11}\text{CO}_2\text{H}$) on template-stripped silver (Ag^{TS});²² the resulting junctions have the form $\text{Ag}^{\text{TS}}/\text{S}(\text{CH}_2)_{11}\text{T}/\text{Ga}_2\text{O}_3/\text{EGaIn}$, where $\text{T} = \text{CH}_3$ or CO_2H , and (ii) a freshly cleaved,

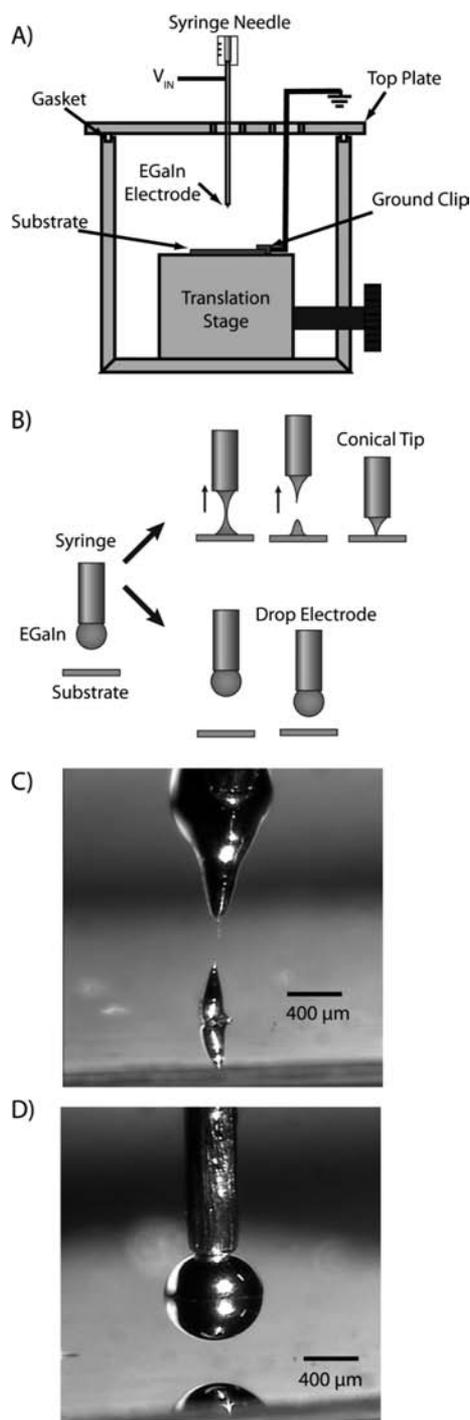


Figure 1. (A) Cross-sectional illustration of the environmental chamber (not to scale); (B) schematic representation of methods to form either a conical-tip or hanging-drop $\text{Ga}_2\text{O}_3/\text{EGaIn}$ electrodes from an extruded drop; (C) microscopic images of a conical $\text{Ga}_2\text{O}_3/\text{EGaIn}$ tip; and (D) microscopic images of a drop electrode. In some instances, during the formation of conical tips a whisker forms (see panel 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.

bare, graphite substrate^{23,24} formed by gluing a highly ordered pyrolytic graphite chip to a metal shim (to form a junction that we describe as $\text{HOPG}/\text{Ga}_2\text{O}_3/\text{EGaIn}$). We also tested two different $\text{Ga}_2\text{O}_3/\text{EGaIn}$ 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 (we believe) has a thinner and more-flexible Ga₂O₃ 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 it 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 Ga₂O₃/EGaIn electrodes are not affected by changes in RH over a range normally encountered in the laboratory. Junctions incorporating carboxyl-terminated SAMs gave current densities at 5% RH that were $\sim 10\times$ lower than those observed at higher RH levels.
- (iv) Junctions using hanging drop electrodes result in higher values of $J(V)$ than junctions using conical tip electrodes by $\Delta \log |J|_{\text{mean}} \approx 2-3$. We attribute this difference in $J(V)$ to differences in surface roughness between the conical and spherical drop electrodes.

■ BACKGROUND

Ga₂O₃/EGaIn Top-Electrode in Molecular Junctions.

We use the Ga₂O₃/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 Ga₂O₃/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, 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 flattened¹ and unflattened²⁻⁴) 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 2–3 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 Ga₂O₃/EGaIn. Under ambient conditions, a thin self-limiting layer of Ga₂O₃ forms very rapidly¹⁶ 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 Ga₂O₃ layer on EGaIn¹ by measuring the resistance of Ga₂O₃/EGaIn electrodes on a HOPG substrate forming a junction with the structure HOPG//Ga₂O₃/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 Ga₂O₃ film was $R_{\text{Ga}_2\text{O}_3} = 3.3 \times 10^{-4} \Omega \text{ cm}^{-2}$. This resistance is lower (by a factor of 10) than the resistance of a SAM composed of the shortest alkanethiolate (SCH₃, SC₁) ($R_{\text{SC}_1} = 1.0 \times 10^{-3} \Omega \text{ cm}^{-2}$).

The electrical²⁹⁻³¹ and physical properties of gallium oxide, and its reactivity toward different chemicals,³²⁻³⁴ are strongly dependent on the method by which it is formed (the Supporting Information briefly discusses the chemical reactivity of gallium oxide). 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 GaAs³¹).

Simeone et al.¹ have compared a liquid drop of Hg and a conical tip Ga₂O₃/EGaIn electrode in measurements of a Fe/FeO_x substrate, where the FeO_x was the most-resistive component of the junction. They created electrodes with equivalent nominal contact areas, and found that the current density of the conical tip electrode was $\sim 10^{-3} \times$ lower than the value measured from the Hg-drop electrode. They concluded that the difference in current density was due to the fact that the Ga₂O₃/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 Ga₂O₃ 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% 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 surface.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 dewetting is plausible at the interface between the SAM and the asperities on the surface of the Ga₂O₃. 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 Ga₂O₃ 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 SECTION

SAMs of Alkanethiolates. We used Ag^{TS} substrates bearing SAMs of *n*-dodecanethiolate (SC₁₂) as the standard (or reference) for comparison; measurements of current density across this SAM are well-characterized and replicable across many users.^{1,3} A template-stripped Ag substrate (Ag^{TS}) was placed in a 3 mmol solution of dodecanethiol (HS(CH₂)₁₁CH₃ in toluene) for 3 h under nitrogen. We also used SAMs bearing a hydrophilic, polar terminal carboxylic acid (SC₁₁COOH) on Ag^{TS}: this SAM, which has a higher affinity for water molecules than does SC₁₂,³⁸ allowed us to study the effect of environmental humidity on measurements of *J*(*V*).

Graphite Substrate for Examining Atmospheric Effects. We chose graphite (SP³ HOPG, SPI, Inc.) as a bottom electrode in some of our studies to provide a flat, well-defined surface that was unreactive toward the Ga₂O₃/EGaIn top electrode, unreactive toward O₂, and hydrophobic.^{39,40} Junctions comprising Ga₂O₃/EGaIn and HOPG result in an ohmic metal/semiconductor interface; that is, the current density, *J*, varies linearly with the applied voltage.¹ 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 (root mean square (rms) 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 Ga₂O₃ film, rather than to some other part of the junction.

Geometries of the EGaIn Electrode. We used two different Ga₂O₃/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 pulling 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 preflattening 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 Supporting Information.

“Selected” Conical Tips. Conical tips are easy to make, and they enable the rapid fabrication of junctions that have a smaller nominal contact area (50–1000 μm²) 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 we 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 they contribute to dispersions in *J*(*V*) data. On average, the creation of a visible-tip asperity occurs in ~4 of every 10 tips formed. In order to avoid the ambiguities associated with such asperities, we examine the tip with a microscope after formation, and selected the conical tips that are free of visible surface irregularities for use. 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 in the Supporting Information shows SEM images suggesting the surface roughness associated with conical tips and spherical drops of Ga₂O₃/EGaIn.

Environmental Conditions. We used dry air from a compressed source (Lot No. AI UZ300, Airgas, Inc.) and generated low-oxygen atmospheres (<0.02% O₂, which is our limit of detection) using argon (99.999% purity, Lot No. AR UHP300, Airgas, Inc.) or N₂ (99.999% purity, Lot No. NI UHP300, Airgas, Inc.). For experiments in low-O₂ atmospheres, we began electrical measurements across the junction once the O₂ sensor (Model R-17D, Teledyne Analytical Instruments) indicated an O₂ concentration value of <0.2% (the minimum detectable reading for the instrument). We generated reactive atmospheres using O₂ and NH₃ gases (O₂, Lot No. OX300 and anhydrous NH₃, Lot No. AM AH35, Airgas, Inc.). 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). 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, O₂, Ar, and N₂) in which it was formed and the junction was measured (Figures 2A–D); in particular, the mean values and standard deviations of log |*J*| (in units of A/cm²) are indistinguishable (log |*J*| = 4.4, σ_{\log} = 0.25). EGaIn drops formed in air and O₂ have surface films of Ga₂O₃, while those formed in N₂ or Ar either do not, or have only a thin or partial film. We therefore conclude that the Ga₂O₃ 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 O₂ and Measured in Air or O₂. Figures 2A and 2B summarize measurements using hanging-drop electrodes formed in O₂-containing atmospheres (air and O₂, respectively) and a HOPG substrate; we assume that the surface of these drop electrodes have a Ga₂O₃ 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-O₂ 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 O₂ concentration in which it is formed, and, as observed previously, it is too small to influence the tunneling currents measured through SAMs.

Junctions using a conical-tip electrode on a HOPG substrate were measured in selected atmospheres of air, argon, and anhydrous ammonia. Figure S5 in the Supporting Information summarizes these data. As we observed with measurements

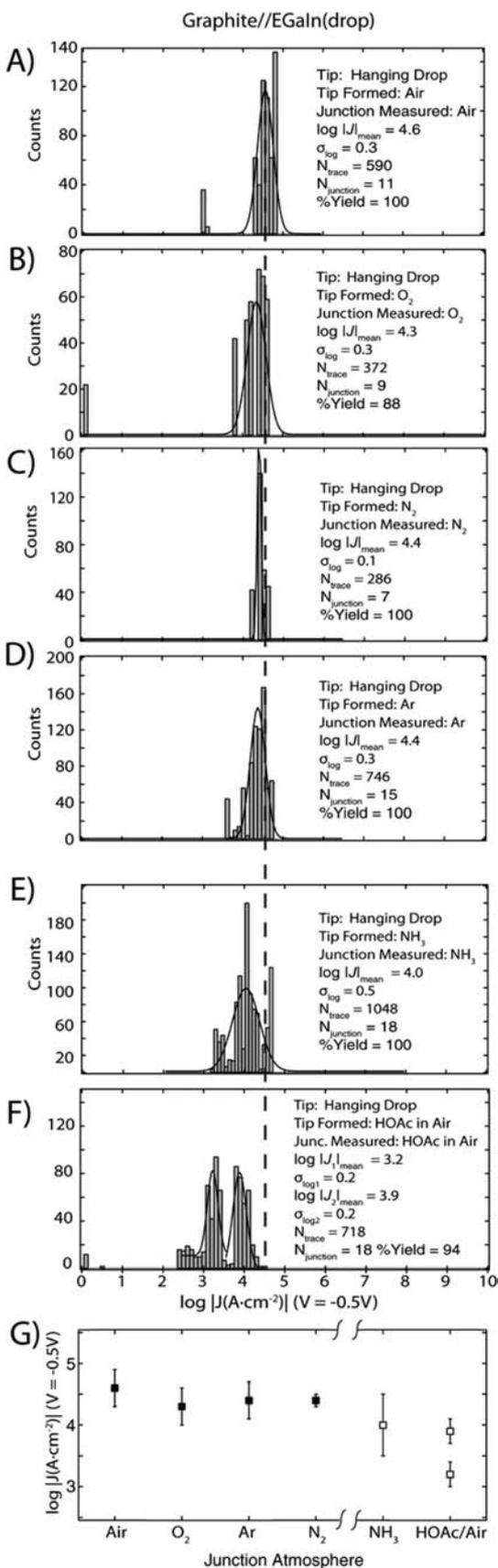


Figure 2. Histograms of the current density of EGaln drop electrode junctions on a graphite substrate. Measurements were collected in an atmospheric chamber where we altered the composition of the environment in which the tips were formed and junctions were

Figure 2. continued

measured. “Tip Formed” represents the atmosphere in which the electrode was formed; “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, and (F) acetic acid in air. Current density values ($\log |J|(-0.5 \text{ V})$) are estimated from Gaussian fit to the histogram. The number of scans (N_{traces}), the number of junctions ($N_{\text{junctions}}$), the mean for $\log |J|$, and the 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 panel G.

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 O₂ 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 $\log |J|_{\text{mean}} \approx 1.3$.

Hanging-Drop Electrodes Formed in Argon or N₂ and Measured in Argon or N₂. Atmospheres of N₂ (Figure 2C) or argon (Figure 2D) contained O₂ concentrations of <0.2%. We believe that the low-O₂ environments resulted in EGaln drops that certainly did not have the same Ga₂O₃ film that normally forms on the surface of EGaln in air, and may only have a partial, or incomplete, thin film. Junctions formed with these electrodes on a graphite substrate had values of $\log |J|_{\text{mean}}$ similar to those formed under air and pure O₂. 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, bends easily, and fractures upon extension. This layer allows the formation of stable junctions with 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 $\log |J|_{\text{mean}}$ seems to be slightly lower than junctions formed under air, O₂, N₂, or argon, 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 N₂ or argon 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 $\log |J|_{\text{mean}}$ 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.

Influence of Gaseous Environments on the Electrical Characteristics of Ag¹⁵S(CH₂)₁₁CH₃/Ga₂O₃/EGaln 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

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 J(-0.5 \text{ V}) $ (A/cm ²)	σ_{\log}	yield (%)	atmosphere of tip formation	atmosphere of junction measurement	$\log J(-0.5 \text{ V}) $ (A/cm ²)	σ_{\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

^aGaussian distribution calculated for data near the mean, excluding anomalous data. ^bThe data seems to have a bimodal distribution.

(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 we again purged the chamber with the atmosphere to be examined.

We were unable to form conical-tip electrodes under either argon or N₂ (Table 1) because, in atmospheres with O₂ concentrations below our limit of detection, the structurally stabilizing oxide film does not appear to 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 $\log |J(-0.5 \text{ V})|$ collected from junctions of conical Ga₂O₃/EGaIn tips formed in air and then used in measuring current densities across a Ag^{TS}/SC₁₂//Ga₂O₃/EGaIn junction in air, O₂, argon, and N₂ showed no significant difference (see Figure 3).

Conical-Tip Electrodes Formed in Air and Measured in Argon, N₂, NH₃, and HOAc/Air. Measurements obtained under a N₂ atmosphere (Figure 3C) provided $\log |J|_{\text{mean}}$ values similar to those measured in air. The majority of measurements in argon (Figure 3D) are also similar, although they include several outlying points near $\log |J| \approx 0.5$ (these points are not included in the Gaussian fitting) and a few points at $\log |J| = +4.2$; the latter are shorted junctions.

The cluster of data at $\log |J| \approx 0.5$ may be a result of junctions in which the Ga₂O₃ film ruptured (see Figure S1C in the Supporting Information, which shows such ruptures) while the tip was in contact with the SAM; in this circumstance, because the concentration of O₂ is low, the gallium oxide film will not reform. The resulting junction, post-rupture, will plausibly have a greater area of effective electrical contact than junctions formed with typically rough conical tips, and thus give a mean value of $\log |J(V)| \sim 2-3$ times greater than that of 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, $\log |J|^{\text{drop}} - \log |J|^{\text{conical}} \approx 1.8$, 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 increase by a factor of $\sim 10^3$ in $J(V)$, relative to the contact area of a conical-tip junction.

Interestingly, junctions measured in the ammonia atmosphere gave values of $\log |J|_{\text{mean}} = +0.4$ (recall Figure 3E)—an increase of ~ 3 orders of magnitude, relative to values in air, O₂, and N₂ (recall Figures 3A, 3B, and 3C) and are approximately the same as the cluster of values observed under argon (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 (see Figure S6 in the Supporting Information). Therefore, we conclude that the ammonia does not damage the SAM. There seem to be at least two possible rationalizations for the behavior in NH₃, 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 Ga₂O₃) 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 argon, 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 argon, is not evident from the available data, although the adsorption of NH₃ 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 Ga₂O₃ and/or the SAM.

Junction Measurements Using Hanging-Drop Electrodes. We also formed junctions using hanging-drop EGaIn electrodes on *n*-dodecanethiolate (SC₁₂)-modified Ag^{TS} substrates (Figure 4). The drops were first formed in air—thus ensuring that they had a Ga₂O₃ 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 ($\Delta \log |J| \approx 1.8$; $|J|^{\text{drop}}/|J|^{\text{conical}} \approx 100$) to an increase in electrical contact area; hanging-drop electrodes have a lower surface

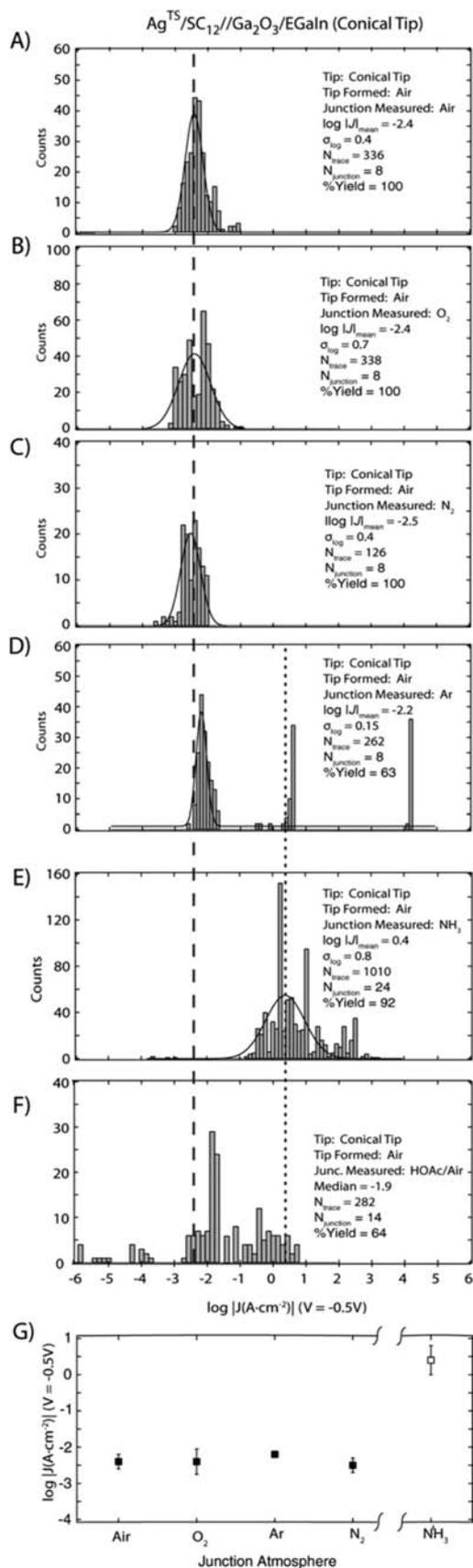


Figure 3. Histograms of current density measured with $\text{Ga}_2\text{O}_3/\text{EGaIn}$ conical-tip electrodes on a SAM of dodecanethiol forming junctions with the structure $\text{Ag}^{\text{TS}}/\text{S}(\text{CH}_2)_{11}\text{CH}_3//\text{Ga}_2\text{O}_3/\text{EGaIn}$. “Tip Formed” represents the atmosphere in which the electrode was formed;

Figure 3. continued

“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, and (F) acetic acid vapor in air. Current density values ($\log |J|(-0.5 \text{ V})$) are estimated from the Gaussian fit to the histogram. The number of scans (N_{traces}), the number of junctions ($N_{\text{junctions}}$), the mean for $\log |J|$, and the standard deviation (σ_{\log}) are presented for each atmosphere. The Gaussian fit for argon (panel D) was measured for the first mode of the data at $\log(J) = -2.2$. No Gaussian was fit to the acetic acid data (panel F). A summary of Gaussian fit data for each atmosphere is given in panel G.

roughness and therefore better conformal contact with the substrate than conical tips. In measurements taken in low- O_2 atmospheres (argon and N_2), we observed an additional increase in current density to $\log |J| = +0.3$ with drop electrodes, resulting in a value of $\Delta \log |J| \approx 2.8$ ($|J|_{\text{drop}}/|J|_{\text{conical}} \approx 1000$). 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 the SAM and the 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 idiosyncratic point during measurements (consisting of 20 J - V scans), and 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 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, because of an increase in the effective electrical contact area.

Effect of Relative Humidity on Measurement of $J(V)$.

We examined the effect of relative humidity (RH) 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 ($\text{HOPG}/\text{Ga}_2\text{O}_3/\text{EGaIn}$, square) and the SAM ($\text{Ag}^{\text{TS}}/\text{S}(\text{CH}_2)_{11}\text{CH}_3//\text{Ga}_2\text{O}_3/\text{EGaIn}$, circle). Junctions having a carboxylic acid-terminated SAM (noted by a triangle in the figure) 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 $\text{SC}_{11}\text{CO}_2\text{H}$ SAMs under ambient conditions gave $J(V) = -2.1$ ($\sim 35\%$ RH), while $\text{SC}_{11}\text{CH}_3$ SAMs gave $J(V) = -1.3$ ($\sim 45\%$ RH), both giving a standard deviation of $\sigma_{\log} =$

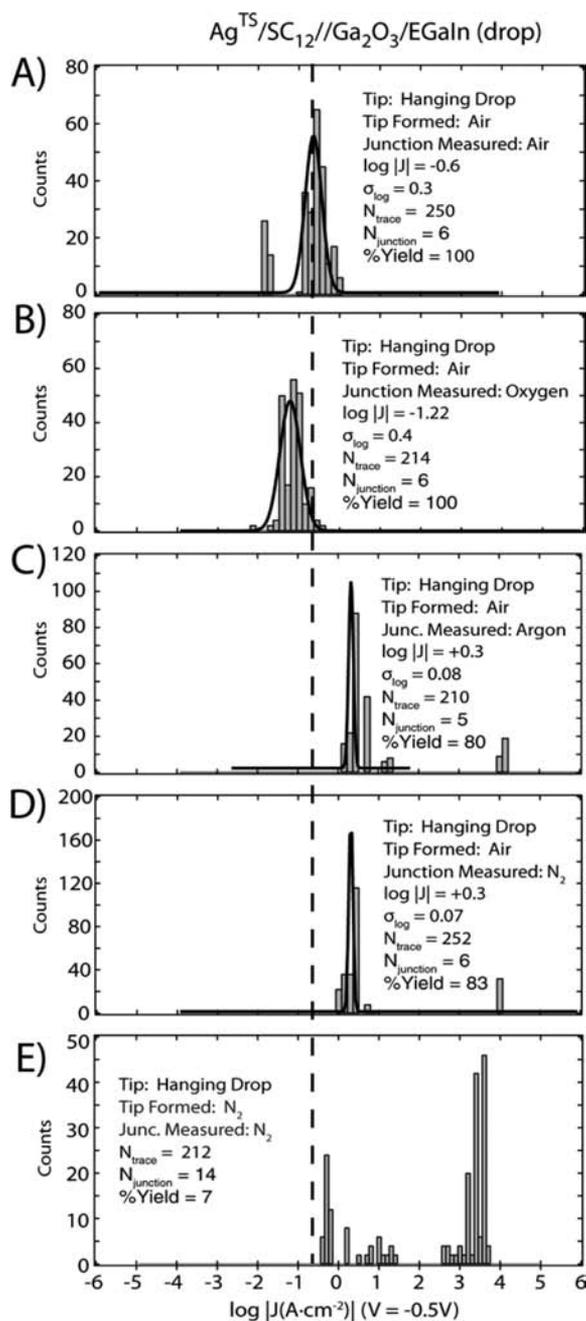


Figure 4. Histograms of current density measured with Ga₂O₃/EGaIn hanging-drop electrodes on a SAM of dodecanethiol forming junctions with the structure Ag^{TS}/S(CH₂)₁₁CH₃//Ga₂O₃/EGaIn. Junctions were formed under (A) air, (B) oxygen, (C) argon, and (D) nitrogen. In addition, panel E displays measurements 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. The number of scans (N_{traces}), the number of junctions ($N_{\text{junctions}}$), the mean for $\log |J|$, and standard deviation (σ_{\log}) are presented for each atmosphere.

0.4; these values are consistent with our measurements (within one standard deviation of the error) and demonstrate that SAMs of SC₁₁CO₂H gives $J(V)$ values lower than those of SC₁₁CH₃. However, we do observe 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

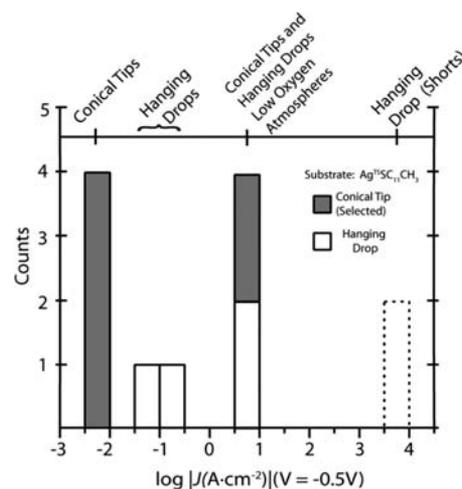


Figure 5. Collection of $\log |J|_{\text{mean}}$ values for Ga₂O₃/EGaIn electrodes, both conical tip and hanging drop, forming junctions on a SAM of dodecanethiol in various atmospheres.

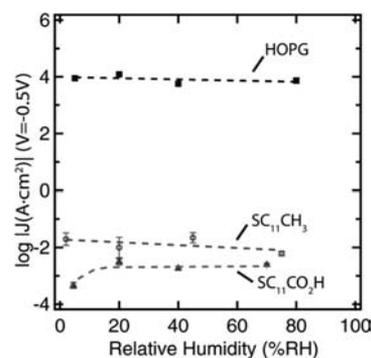


Figure 6. Plot of influence of humidity on the current density of conical-tip Ga₂O₃/EGaIn electrodes on HOPG graphite (denoted by the square symbol), Ag^{TS}/S(CH₂)₁₁CH₃ (denoted by the circle symbol), and Ag^{TS}-S(CH₂)₁₁COOH (triangle) substrates. Measurements were performed in a humidity-controlled atmospheric chamber. A hanging-drop electrode was used on the graphite substrate, and a conical-tip electrode was used on the SAMs.

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 in the Supporting Information).

CONCLUSIONS

We had two objectives in this work:

- To investigate the influence of different environmental conditions (i.e., different gases surrounding the Ga₂O₃/EGaIn tip and the junctions at room temperature) on the fabrication of the tip, and on the measured current densities, $J(V)$, across the tunneling junctions.
- To study the influence of the surface roughness associated with the Ga₂O₃ on measurements of $J(V)$ by comparing results obtained with the rougher conical tip and the smoother, although less stable, hanging drop.

The oxide can influence the performance of the junction in two ways: (i) by acting as a resistive element in the junction or (ii) as a mechanical influence by determining the effective electrical contact area of the junction. We find that the oxide

does not significantly contribute to the resistance of the junctions, but does influence the area of electrical contact.

We summarize our findings in four points.

- *The Ga₂O₃ film does not contribute to the resistivity of the junction.* Junction measurement on graphite using hanging-drop electrodes formed under N₂ or argon (presumably with little or no oxide film) demonstrated current densities similar to measurements made with hanging-drop electrodes formed in the presence of O₂, possessing a film of Ga₂O₃ on the electrode surface (recall 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 (argon, N₂) or O₂-containing (air, O₂) atmospheres. For these measurements, the conical tips were first formed in air (ensuring a Ga₂O₃ 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 the adsorption of ammonia to the oxide film, or some other interaction with the gas.

The use of electrodes with thicker or thinner Ga₂O₃ 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 Ga₂O₃ 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 Ga₂O₃ film on the EGaIn electrode influences junction stability.* The presence of the Ga₂O₃ film increase the yield of working electrodes (>70%) and the presumed reproducibility of the area of electrical contact with the bottom substrate, thus contributing to the generation of reproducible values of $J(V)$, with standard deviations of $\sigma_{\log} \approx 0.3$. Junctions consisting of conical-tip and hanging-drop electrodes created in air, and measured in O₂-containing atmospheres, had working yields of 100%. For junctions measured in low-oxygen atmospheres, the working yield decreased to a range between 60% and 85%. This decrease suggests that the presence of oxygen contributes to improved electrode performance and to reproducibility in $J(V)$ measurements, as measured by low values of σ_{\log} , 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 Ga₂O₃/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 mechanical stability and reproducibility of $J(V)$ measurements within 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 (<5% RH), 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 Ga₂O₃ film (see Figure S7 in the Supporting Information). At low humidity, there is no or little water layer(s) adsorbed on the surfaces of the Ga₂O₃ and the CO₂H-terminated SAM. The surface free energy of the CO₂H-terminated SAMs (unlike that of methyl-terminated SAMs) may induce the formation of a water layer onto its surface at higher values of RH. We used deionized water for the production of humid air; therefore, we do not expect the chemisorption of metallic ions. If transition-metal ions were present, it is possible that the junction measurements could be influenced by electron transfer to those species under an applied bias.

- *Surface roughness of 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 Ga₂O₃ of conical tips has a significant, but unquantified, roughness (see Figures S1A and S1B in the Supporting Information). Formation of the drop electrode, on the other hand, does not require this rupture, and is therefore smoother (see Figure S1C in the Supporting Information).

The oxide film on the hanging-drop electrode seems more flexible and thinner than that formed on the conical electrode. These characteristics (or others) result in higher values of $J(V)$ than those obtained with a conical tip for the same SAM: measurements across a C₁₂ SAM in air give values of $\log |J|_{\text{mean}} = -2.4$ for a conical tip and $\log |J|_{\text{mean}} = -0.6$ for a drop electrode; $\Delta \log |J| \approx 1.8$ (e.g., $|J|_{\text{drop}}/|J|_{\text{conical}} \approx 100$). The only difference that we have identified between these two measurements is the roughness of the Ga₂O₃ film, and, thus, the electrode surface. When we compare measurements in the N₂ 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 ($|J|_{\text{drop}}/|J|_{\text{conical}} \approx 1000$). 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 FeO_x/Fe substrate gave $\sim 10^3$ 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.

■ ASSOCIATED CONTENT

📄 Supporting Information

Ga₂O₃ 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 degradation in AcOH atmosphere; $J(V)$ histogram of conical tips on graphite substrates in air, Ar, and NH₃; $J(V)$ of single electrode exposed

to air, NH₃, air again; schematic of humidity interacting with oxide surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gwhitesides@gmgroup.harvard.edu.

Notes

The authors declare no competing financial interest.

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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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