

The 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

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Minor discussions

Properties of Gallium Oxide

Gallium oxide is a transparent insulating material that is often used in the production of semiconductor devices, in catalytic devices, and in gas sensors. Permanent functionalization of the oxide is difficult, however, due to the high stability of the β -Ga₂O₃(100) surface.¹ The standard method of functionalization relies on the reactivity of the surface hydroxyl (–OH) groups, which form naturally on air-exposed oxide surfaces. Although generally chemically inert at room temperature, adsorption or physisorption of adventitious species may change the mechanical and/or electrical properties of the oxide film.

Reactivity of Ga₂O₃ with acid

Exposure of Ga₂O₃/EGaIn to an acidic aqueous solution (HCl, pH < 3) dissolves the oxide from the surface and, in the case of hydrochloric acid (HCl), prevents further oxidation of the metal surface.² Removal of the oxide film affects both the wetting³ and mechanical properties⁴ of the EGaIn metal.

Kim et al.³ reported that the contact angle of EGaIn drops on several substrates (glass, CytopTM-coated glass, and TeflonTM) increased upon exposure to vapors of HCl. Using X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering (LEIS), they found that the surface of the drops had changed from predominantly gallium oxide and indium oxide, to gallium chloride (GaCl₃) and indium chloride (InCl₃).

Under normal conditions, where a native oxide is present on the EGaIn surface, drops exhibit non-Newtonian behavior and can be deformed into arbitrary shapes under an applied stress. Xu et al.⁴ found—after submerging drops of EGaIn in aq. HCl (> 0.2 M)—that the EGaIn drops could not be deformed permanently; they return to spherical shapes upon removal

of applied stress. A pendant drop method indicated that the presence of the oxide film increased the apparent surface tension of suspended drops of EGaIn (compared to the pure liquid alloy).

Weak acids, such as methanol or acetic acid, physisorbed on the gallium oxide surface, rather than dissolving the oxide layer. Hydrogen bonding played an important role in the stability of the adsorbed and physisorbed species on the oxide. Bermudez¹ found that the physisorption of H₂O or methanol (CH₃OH) was weakly exothermic, while chemisorption—due to dissociation of the O–H bond—was weakly endothermic. The author found that when alcohol (1-octanol) saturated surfaces were exposed to acetic acid (in the vapor phase), a large fraction of the alcohol was displaced by acid.¹ When a Ga₂O₃ surface was first saturated with acetic acid, exposure to H₂O or alcohols did not displace or hydrolyze the surface, this observation confirms that the acid is more strongly bound to the oxide surface than water or alcohol.

Reactivity of Ga₂O₃ with Ammonia

Previous studies^{5,6} reported the influence of chemisorbed basic atmospheric molecules (NH₃, NO₂, NO, SO₂) on the surface acidity of an Al₂O₃-Ga₂O₃ systems, where gallium oxide was loaded on an alumina support. Using microcalorimetry,⁵ Gergely et al. reported that NH₃ strongly adsorbs to the gallium oxide surface. In this study, surface acidity and basicity were measured using gas phase adsorption microcalorimetry: Gergely et al. measured a slight decrease in acidity and attributed it to NH₃ adsorption onto the oxide.

Standard EGaIn Electrode Formation: Conical Tip

A drop of EGaIn is extruded from the syringe and brought into contact with a metal substrate (often silver or gold) to the point where the drop adheres. The syringe is withdrawn

from the substrate causing elongation of the drop into an hour glass shape. During this manipulation the EGaIn structure breaks, leaving a conical tip electrode on the syringe.

Pre-flattened EGaIn Conical Tip Electrodes

“Pre-flattened” conical tips are another tip fabrication method that can be used, although it was not used in environmental chamber measurements. These tips—described in detail in reference 1—are generated using a procedure similar to that used with conical tips, with an added step. Once a conical tip is formed, it is brought into contact with a clean silicon wafer to the point where the contact interface reaches the desired geometry (or cross-sectional diameter); it is held in this position, and a bias of 1-2 V is cycled between the tip and substrate. This method, we presume, eliminates whiskers and may reduce other sources of roughness. After cycling, the tip is withdrawn from the substrate and used in generating junctions on the SAM.

Experimental Details

Environmental Chamber Design

The test chamber (1.27 cm thick acrylic plexiglass) has an inlet tube connected to several three-way valves, which allowed us to change the atmosphere in the chamber (Figure S2). EGaIn was introduced into the chamber using a syringe needle through a rubber septum on the lid. The needle was attached to a micromanipulator (outside the chamber) allowing multi-axis motion of the needle tip. A rotary screw on the substrate stage allowed one-axis motion of the substrate, which permitted the formation of junctions in different locations without opening the chamber. A stainless steel wire pierces a second septum and connects to a retaining clip for the substrate and serves as a ground electrode for the junction.

Gas lines feeding into the test chamber from the gas cylinder consist of copper tubing and brass fittings. The outlet lines from the test chamber that feed into the fume hood are Tygon tubing. We maintained a positive pressure on the feed gas to prevent backfilling from room air or the gas outlet tube. The lid gasket consists of an expanded Teflon gasket, allowing movement of the lid without breaking atmosphere.

All gasses were supplied by Airgas East (Cambridge, MA). A commercial ultrasonic humidifier (Model V5100NS, Proctor and Gamble, Cincinnati, OH) was used to generate humid room air for humidity experiments. Oxygen concentration was measured with Model AD300 controller with a R-17D sensor from Teledyne Analytical Instruments.

Operation of the Environmental Chamber

The test chamber was purged with clean dry air from a compressed source (flow rate of ~995 mL/min for 5 minutes) to remove ambient air from the chamber; the gas flow rate was reduced to maintain positive pressure in the chamber.

An EGaIn filled microsyringe was loaded into the chamber through the septa in the lid. A drop of EGaIn (~0.5 μ L) was extruded from the syringe and immediately discarded (removing any contaminants or oxide on the syringe during filling), and a new drop was extruded to be used as a top electrode. Electrode formation is described below.

In cases where we first made a tip in an atmosphere of air, then changed the atmosphere to another gas, we changed the gas stream within several seconds of the tip formation. The time for the new gas to condition the environment varied; in cases where we were able to measure the oxygen concentration this process would take between 3-5 minutes at the flow rates used for the system to read minimal oxygen levels (the metric used for determining the change of the atmosphere for the tips). We allowed 10 minutes from the change of the new gas to the

measurement of the junction to ensure that the junction was formed in a properly conditioned atmosphere. If the tip did not show signs of shorting or failure, it would be used to measure multiple junctions, thus the total exposure time of tips in these environments were varied.

Humidity Measurements

A VWR hygrometer was inserted into the chamber to measure the relative humidity (%RH), when needed. Compressed air was fed into the chamber at 995mL/ min until the hygrometer read ~5% RH. The compressed air was then shut off and the humidifier was turned on until the humidity reached test conditions (25, 40, and 60% RH); once reached, the humidifier was turned off. A volume of ~ 0.5 μ L of EGaIn was extruded and discarded, and a new drop was extruded to form the top electrode.

Acetic Acid Doped Air Atmosphere

An acetic acid atmosphere was created by placing an open vial containing glacial acetic acid (~ 4 mL) in the chamber, closing the lid, and blowing clean, dry air (from a compressed source) through the chamber for five minutes at a rate of ~20 mL/min. We stopped the air flow and waited five minutes for the acetic acid to evaporate before proceeding with electrode formation and junction measurements.

We were unable to maintain a mechanically stable conical tip electrode in the acetic acid doped air environment; therefore we measured the current density as soon as the conical tips were formed. The mechanical instability of a conical tip in an acetic acid atmosphere is displayed in Figure S3.

SAM Preparation

A template-stripped Ag substrate (Ag^{TS}) was placed into a 3 mmol solution of dodecanethiol ($\text{HS}(\text{CH}_2)_{11}\text{CH}_3$) (for alkanethiols we used toluene as the solvent, for carboxyl-terminated SAMs we used ethanol as the solvent). The substrate was held in solution for three hours to allow adequate time for the SAM to form. The substrate was subsequently removed from the solution using clean tweezers, rinsed with filtered toluene and ethanol, dried in air, and then loaded into the test chamber under the retaining clip.

Surface Characterization

XPS Sample Preparation

To create EGaIn films for X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha XPS) analysis we deposited a drop of EGaIn on a clean glass slide and used the edge of another slide to smear the EGaIn drop into a film.

We created several of these EGaIn films and exposed them to ambient laboratory conditions, ammonium hydroxide, and acetic acid vapor. We exposed the samples to these atmospheres by placing the EGaIn films into a sealable container containing a small vial of glacial acetic acid or ammonium hydroxide (2 ml) for 15 minutes. The samples were removed and individually stored in slide carriers until XPS analysis.

XPS Analysis

We acquired the survey spectra using a pass energy of 200 eV, and high resolution, regional scans at a pass energy of 50 eV; elemental quantification was carried out with commercial analysis software (CasaXPS).

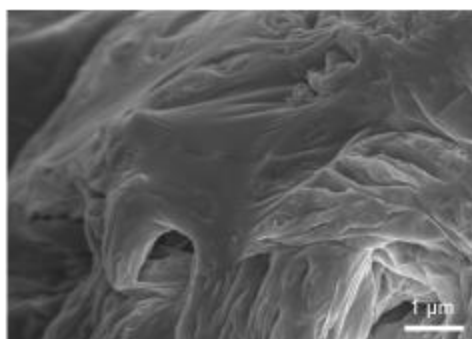
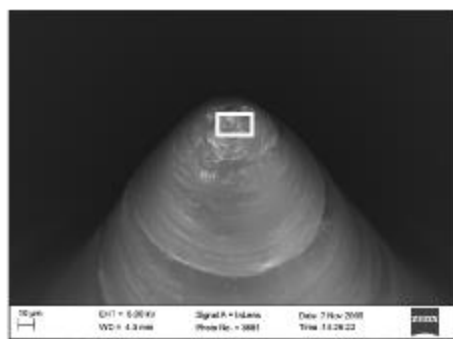
Figure S4 shows the high resolution region scans of Ga 3d and O 1s on the oxide film exposed to ambient conditions (A,B,C) and acetic acid vapor (D,E,F) atmosphere. The peak assignments are consistent with previously reported literature values.

High resolution scans of gallium (Ga 3d) on the oxide film exposed to ambient conditions revealed Ga^0 (~16.9 eV), which we associate with the EGaIn alloy and Ga^{3+} (~19.1 eV) which we associate with Ga_2O_3 (Figure S4 A,D). For indium (In 3d), we observed a value for In^0 (~15.2 eV), which we associate with the EGaIn alloy. High resolution region scans of the oxygen (O 1s) region of the spectrum revealed two distinct oxygen species for the ambient sample (Figure S4B). We attribute the first peak (529.6 eV O 1s) to the oxides of gallium and indium, and we attribute the second peak (530.9 eV) to the hydroxyl groups formed on the inorganic oxides in the presence of moisture.

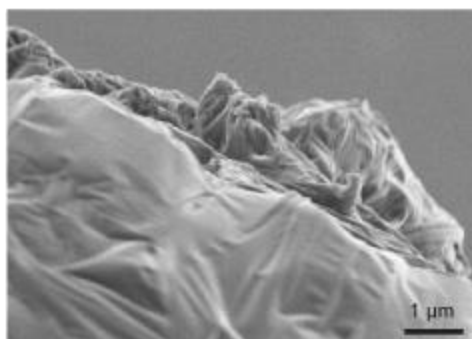
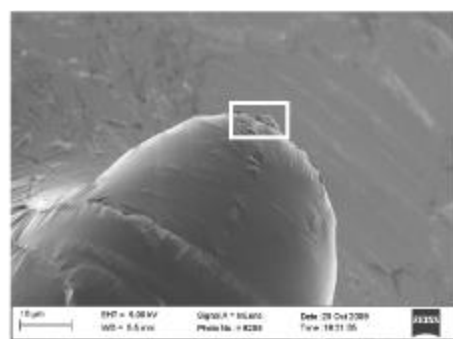
The film exposed to acetic acid demonstrates significant differences to the XPS spectra compared to ambient sample. High-resolution scans of Ga 3d (Figure S4D) revealed a decrease in the Ga^0 signal (~17.2 eV). The Ga^{3+} signal (~20.1 eV) is predominately associated with the Ga_2O_3 film.⁷ We also observed a peak shift (~17.2 eV to ~20.1 eV) compared to the control sample, suggesting a change in the chemical bonding state on the oxide. Moreover, we no longer observe an indium signal, possibly due to physisorption of acetic acid (thickness was greater than the penetration depth of the X-ray; ~10 nm) onto the oxide film (Figure S4A). The single peak in the O 1s spectra for this sample (Figure S4E) is indicative of surface hydroxyl groups (531.6 eV).

Figure S1. SEM images of conical (**A,B**) and spherical drop (**C**) structures of EGaIn. To form the conical structures, we formed conical tip electrodes on a metal substrate. The structures present are the bottom portion of the EGaIn during conical tip formation. We extruded a drop of EGaIn on a silver substrate to form the structure in **C**. Due to unknown reasons, the oxide skin of the drop ruptured while inside the SEM chamber (pumped down to 10^{-7} torr). This demonstrates that we can expose metallic EGaIn, when the drop, or tip, is mechanically damaged. Inset squares represent approximate regions where the high magnification image was taken.

A)



B)



C)

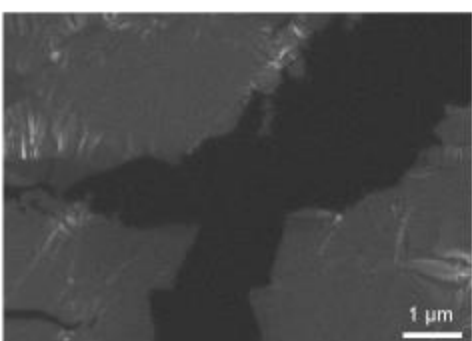
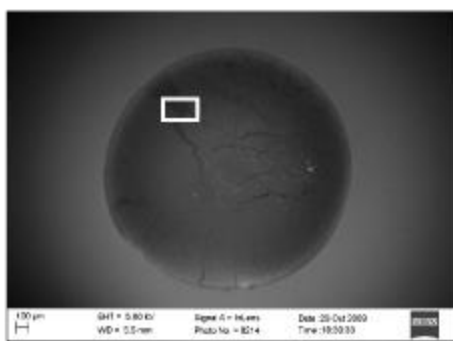


Figure S2: Photographs of the environmental test chamber with removable humidity sensor attached displaying the front (A) and top views (B).

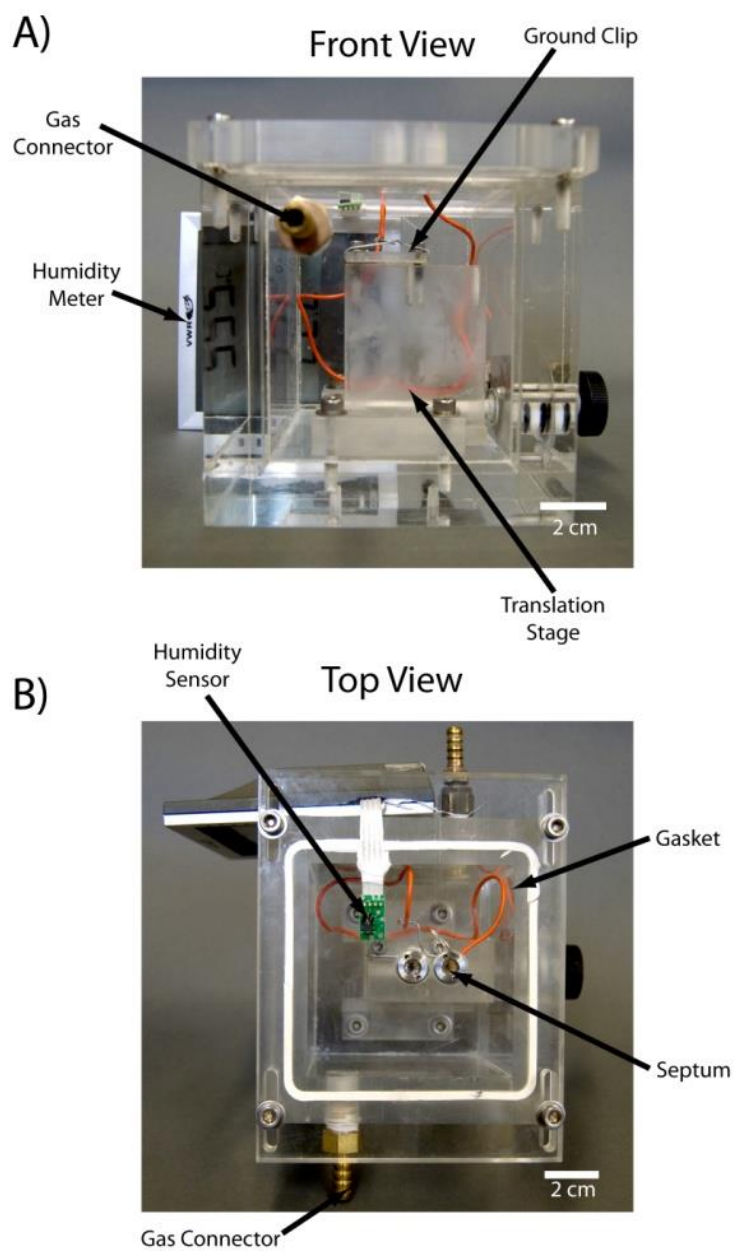


Figure S3. Sequential images of a conical EGaIn tip in an acetic acid environment. The conical tip changes into a spherical drop within 60 seconds as the oxide reacts within the environment. Scale bar is 400 μm . This change occurs both when the tip is held within the environment, and when the tip is used as an electrode in the junction, leading to instability in the junction measurements.

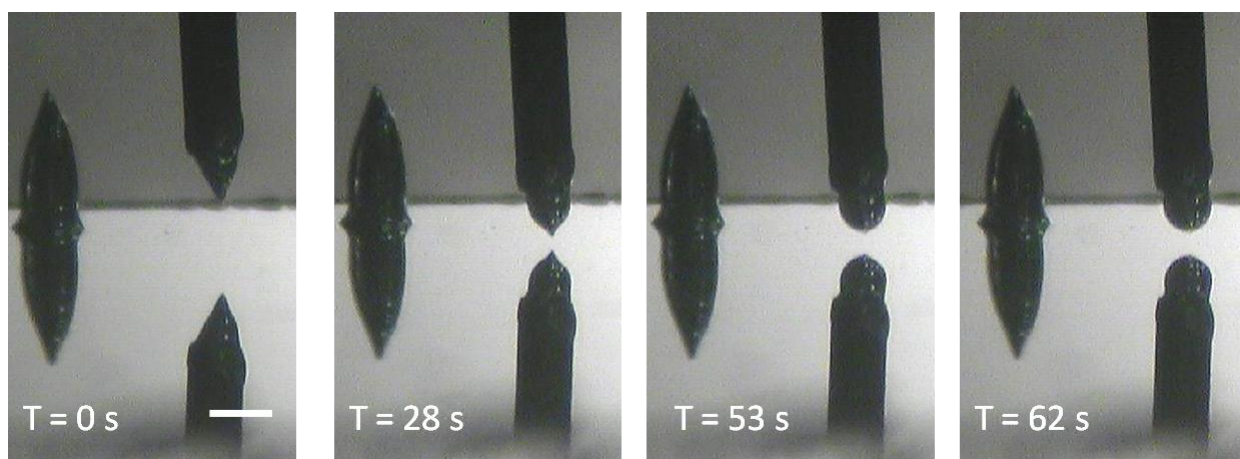


Figure S4. High resolution XPS spectra of the Ga 3d/In 4d region and O 1s region of EGaIn films under ambient conditions (A,B,C) and after exposure to acetic acid vapor (D, E, F). The Ga 3d/ In 4d region indicates of the acetic acid exposed surface (D), the Ga oxide and Ga metal peaks are shifted up stream from their counterparts on the control sample (A), indicating a new bonding states following exposure to acetic acid, additionally there is no In metal peak in this spectra. The O1s spectra of the acetic acid exposed substrate (E) does not display a metal oxide peak, indicating only hydroxyl oxygen species on the surface.

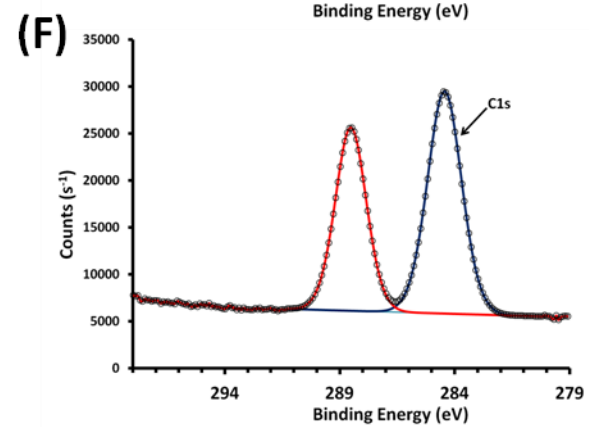
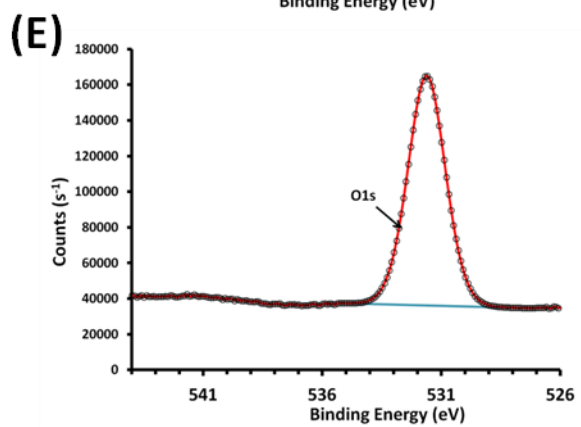
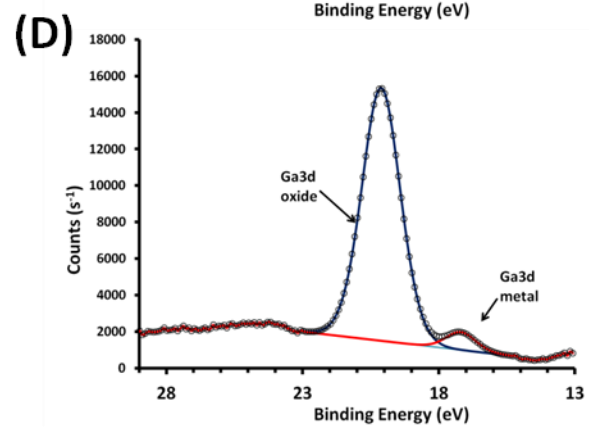
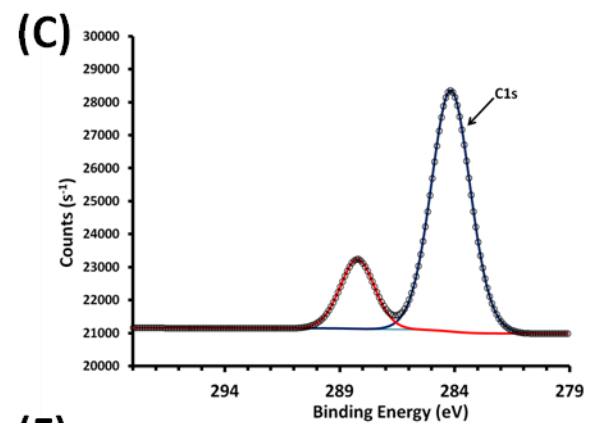
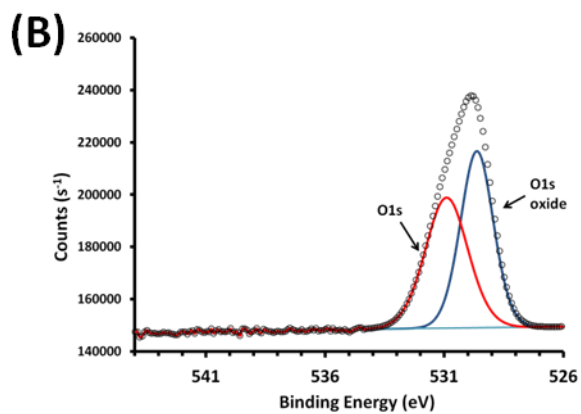
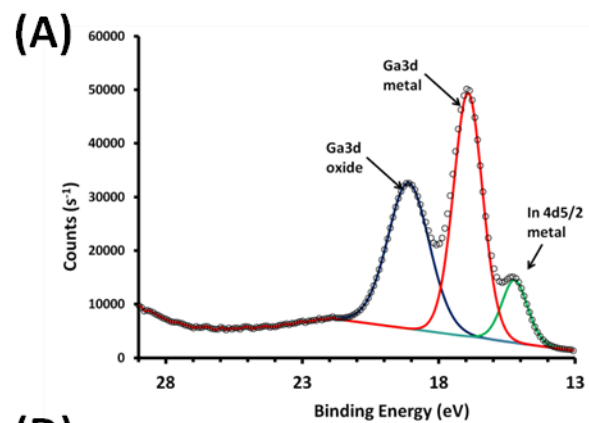


Figure S5. Histograms of the current density of $\text{Ga}_2\text{O}_3/\text{EGaIn}$ conical tip electrodes junctions on a graphite substrate. The histograms (where calculated) are for $\log |J(-0.5\text{V})|$ and $\log \sigma$ for air (A), argon (B), and ammonia (C).

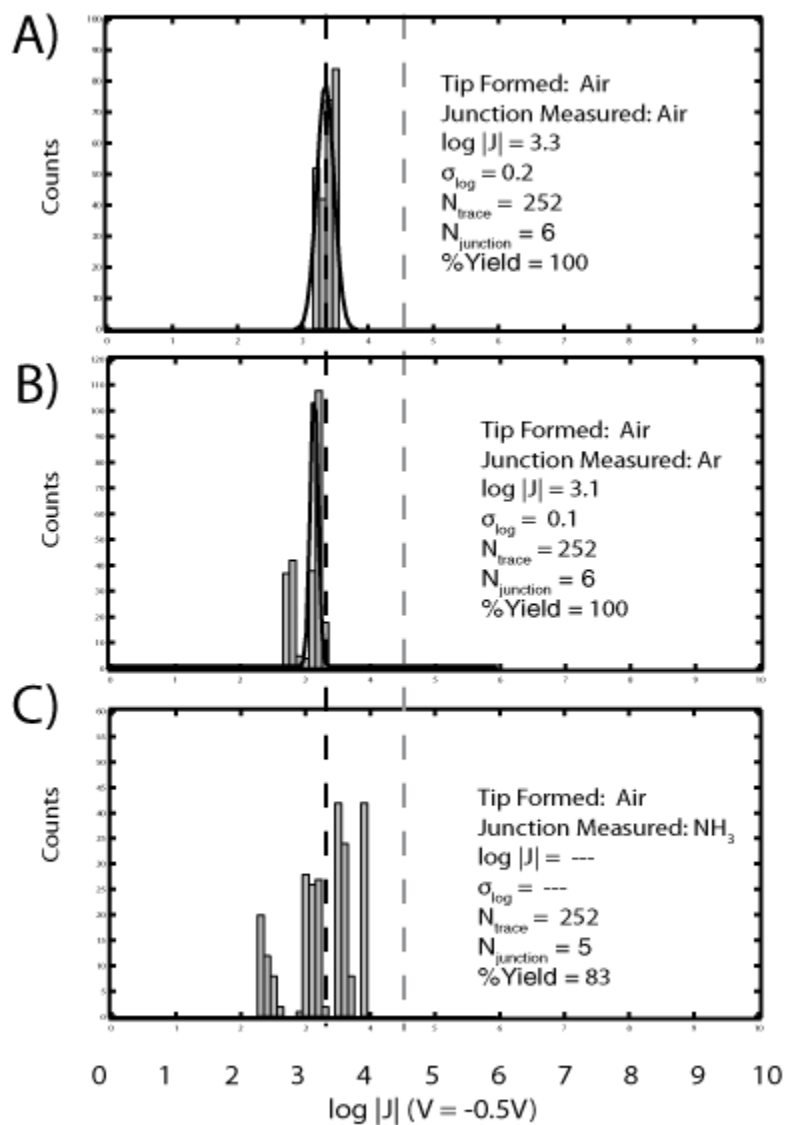


Figure S6. Current density measured on a C₁₂-SAM measured with a single electrode. The reference measurements are made in an air atmosphere. Next the tip is withdrawn from the substrate, and the chamber is purged with ammonia and new junctions are measured. The tip is again withdrawn, followed by a purge of the chamber with air. Using the tip, junctions are again measured in the air environment.

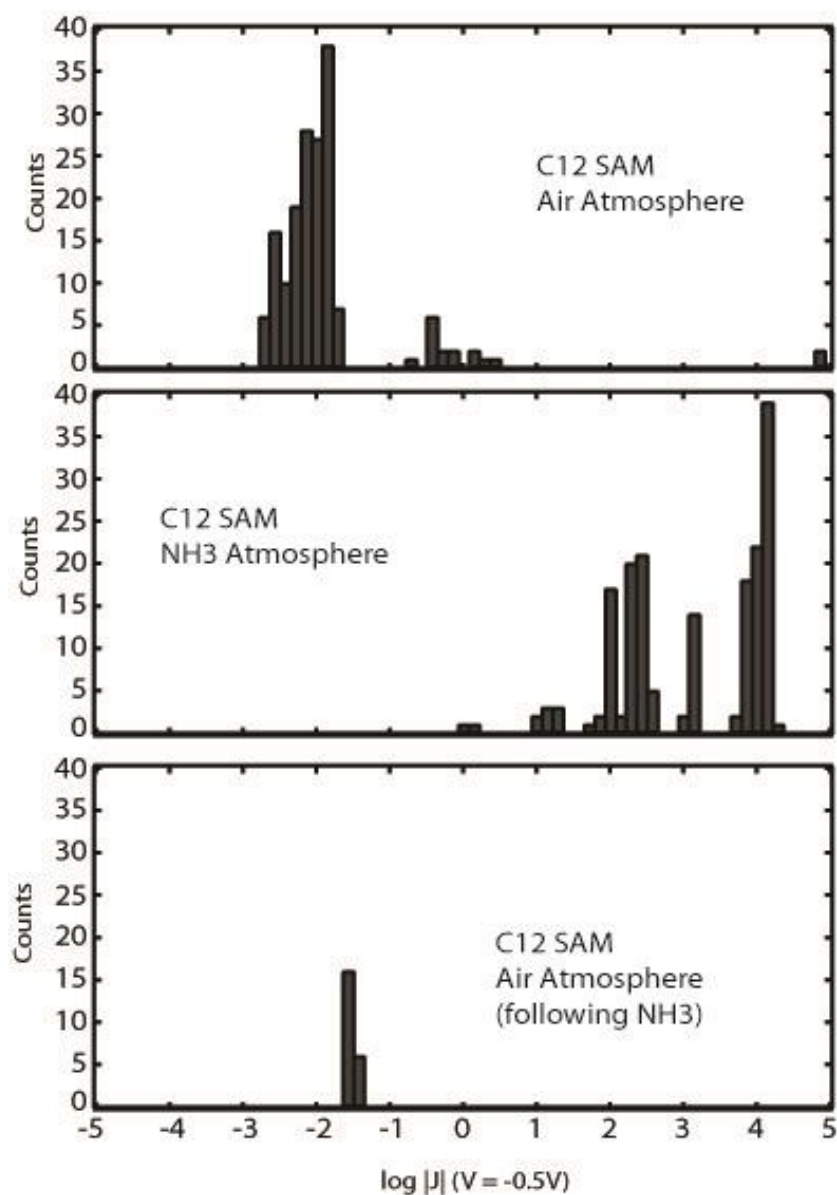
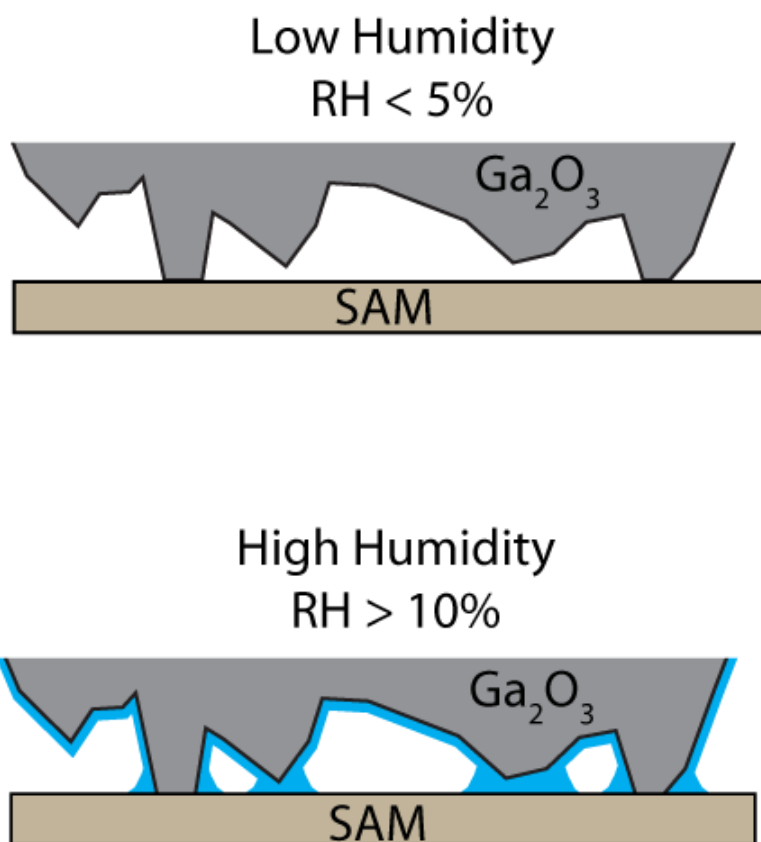


FIGURE S7. Schematic of the potential influence of humidity on performance of the junction.

In a humid ($RH > 10\%$) environment a monolayer of water forms on the SAM and on the electrode, and increases an area of electrical contact.



References

- (1) Bermudez, V. A. *Langmuir* **2008**, *24*, 12943.
- (2) Zrnic, D.; Swatik, D. S. *Journal of the Less-Common Metals* **1969**, *18*, 67.
- (3) Kim, D.; Thissen, P.; Viner, G.; Lee, D. W.; Choi, W.; Chabal, Y. J.; Lee, J. B. *ACS Appl. Mater. Interfaces* **2013**, *5*, 179.
- (4) Xu, Q.; Oudalov, N.; Guo, Q. T.; Jaeger, H. M.; Brown, E. *Physics of Fluids* **2012**, *24*.
- (5) Gergely, B.; Redey, A.; Guimon, C.; Gervasini, A.; Auroux, A. *Journal of Thermal Analysis and Calorimetry* **1999**, *56*, 1233.
- (6) Petre, A. L.; Perdigon-Melon, J. A.; Gervasini, A.; Auroux, A. *Topics in Catalysis* **2002**, *19*, 271.
- (7) Cademartiri, L.; Thuo, M. M.; Nijhuis, C. A.; Reus, W. F.; Tricard, S.; Barber, J. R.; Sodhi, R. N. S.; Brodersen, P.; Kim, C.; Chiechi, R. C.; Whitesides, G. M. *J. Phys. Chem. C* **2012**, *116*, 10848.