Supporting Information

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Experimental Details

**The Nature of the Surface of EGaIn.** To determine the chemical composition of the skin of EGaIn under different conditions, we used Auger spectroscopy (Physical Electronics Model 660 Scanning Auger Microscope) to analyze samples of EGaIn i) as purchased (straight from the bottle), ii) after “in situ” sputtering with argon (that is, we sputtered the EGaIn without removing it from the high vacuum conditions—~5 × 10⁻⁹ torr—found within the chamber of the spectrometer), and iii) after exposure to air for approximately one minute after sputtering. We compared the measured elemental ratios on the surface versus those in the bulk (1:5 atomic ratio of In:Ga. Figure S1 contains the Auger spectra from these three samples, along with the relative atomic percentages of In, Ga, and O in each sample.

The “as purchased” EGaIn showed an enhanced amount Ga and O at the surface (atomic % ratio In:Ga:O = 1:15:17) compared to the bulk, suggesting that the skin primarily consists of oxides of gallium; this result is consistent with the fact that Ga is highly reactive towards oxygen at room temperature. This finding is also consistent with previous studies: X-ray studies on pure
Ga, the majority component of EGaIn, and galinstan—a eutectic alloy of 68.5% Ga, 21.5% In, and 10% Sn by weight that is also a liquid at room temperature—showed that both materials formed a skin of gallium oxide after even a brief exposure to air (180 L of oxygen, where 1 L = 10⁻⁶ Torr s), and that the oxide skin formed a highly uniform passivating layer that protected the bulk material from further oxidation (much like aluminum).

A prior X-ray study of EGaIn—done under ultra-high vacuum—showed that the top monolayer of the EGaIn surface became enriched with In after the ambient skin was sputtered off (this result is reasonable since In has a lower surface energy than Ga by ~30%). We performed Auger spectroscopy on EGaIn after in-situ sputtering and also found that the skin became enriched with In (atomic % ratio In:Ga:O = 5:6:1). Indium has been shown to cover as much as 94% of the surface of EGaIn after sputtering in ultra-high vacuum, but, unlike Ga, In is slow to oxidize when it is exposed to oxygen. When the indium does oxidize, however, it does not form a passivating layer on the surface of EGaIn. We sought to test if the surface of the EGaIn reverts back to the initial state (i.e., enriched with Ga and O) by exposing the as-sputtered EGaIn to ambient air. Indeed, the surface of the EGaIn—after exposure to ambient air for one minute—returned to a state enriched with gallium and oxygen (atomic % ratio In:Ga:O = 1:10:14). The observation that gallium oxide dominated the surface of EGaIn after the sputtered surface was exposed to air implies that either i) the monolayer of In was permeable to oxygen, such that gallium near the surface oxidized and then displaced In at the surface, or ii) oxygen reacted with the small amount of gallium in the monolayer, oxidized gallium, and gallium oxide then displaced In at the surface. Regardless of the mechanism, these results suggest that in the presence of air (i.e., in the ambient) the surface of EGaIn will be predominately covered with oxides of gallium.
Our conclusion that a surface oxide (in particular, gallium oxide) is responsible for the rigid skin agrees with previously reported measurements of the surface tension of a pendant drop of EGaIn: The surface tension of EGaIn at ambient conditions is ~624 mN/m, whereas the surface tension of EGaIn during exposure to aqueous HCl (which presumably causes acid-promoted dissolution of the oxide) is ~435 mN/m. The high surface tension of EGaIn measured under ambient conditions may therefore be explained by the presence of a surface oxide that is capable of supporting more weight from a pendant drop.

**Formation of SAMs of n-Alkanethiolates on Ultraflat Ag.** We obtained ultraflat, substrates of thin (ca. 600 nm) films of silver metal on a polymer (a highly cross-linked polyurethane) supported by a glass slide, by delaminating an evaporated film of silver from an Si/SiO₂ template (the “mechanical template-stripping” procedure), as described in detail elsewhere. Within 10 seconds of cleavage of the Ag films from their templates, we submerged them in a 1-mM solution of the appropriate alkanethiol in ethanol. The substrates incubated in the thiol-containing solution under an Ar atmosphere at room temperature for 8-12 hours. Immediately before use, we removed the substrates and placed them in a vial of fresh ethanol (ca. 20 mL), and gently agitated the vial for one to two minutes, placed them in another vial of fresh ethanol for another one to two minutes (to ensure that any residual adsorbed organics were removed), and dried them under a stream of dry nitrogen.

**Electrical Measurements on SAMs of n-alkanethiolates on Ag.** The conformal top contact was formed by bifurcating a drop of EGaIn between a needle and a clean film of Ag, bringing the resulting conical tip down onto the surface of the SAM. A wire directly attached to the metal needle on the syringe connected the EGaIn electrode electrically with an electrometer (Keithley
The supporting Ag substrate served as the common (ground) electrode by means of a gold needle that penetrated the SAM and contacted the Ag directly. A triaxial cable connected the two electrodes to an external amplifier. The electrometer applied a bias, $V$, across the junction. A positive value of $V$ corresponded with EGaIn being biased positively with respect to the Ag. The entire setup, except the source-meter was housed in a home-built aluminum Faraday cage. The data are summarized in Figure S2.

**Explanation for the Log-Normal Distribution in $J$**

We have previously attributed the log-normal distribution of $J$ (Figure 2) through Ag-SC$_n$/C$_n$S-Hg junctions to the exponential dependence of $J$ on a physical parameter that is distributed normally, such as the effective distance the electron tunnels through the junction, $d$. We ascribed the variation in $d$ to the presence of defects—specifically, defects in which the EGaIn contacted non-terminal carbons in the SAM, so-called “thin regions” of the SAM.$^8$ Current through these thin regions is higher than that through defect-free regions.

We believe that the same analysis applies to the EGaIn junctions. The “outliers” in the histograms in Figure 2 were always, on average, higher values of $J$ than were encompassed by the Gaussian, and were only observed in the junctions containing the longer-chain alkanethiolates SC$_{14}$ and SC$_{16}$. We therefore suspect that these data result from the penetration of EGaIn into defects that are characteristic of more crystalline SAMs, such as grain boundaries. These same defects did not result in artificially high values of $J$ in Hg junctions because they instead caused the junction to short; shorts immediately preceded amalgamation of the Hg and the Ag. We have termed this phenomenon “high-$J$ filtering”.$^8$ Figure S3 shows representative
data for a Hg-drop junction including the initial low-$J$ trace that, upon expulsion of solvent from the SAM, increases and eventually fails via high-$J$ filtering.
Figure S1. Auger spectra (recorded at a pressure of ~5 × 10⁻⁹ torr) of samples of EGaIn i) from the bottle (black line), sputtered with argon within the high vacuum chamber of the spectrometer to remove the outer crust (blue line), and iii) sputtered within the vacuum chamber, and then exposed to ambient air for one minute before being transferred back into the vacuum chamber (red line). The relative atomic concentrations of In, Ga, and O within each sample are listed at the bottom right of the figure. The spectra i) and iii)—the two samples whose surface was exposed to air—are nearly indistinguishable (both indicate the presence of an oxide of gallium at the surface of EGaIn), and spectrum ii) shows a surface enriched with In—that is, the observed ratio of (5:6, In:Ga) is greater than that present in the bulk of the eutectic (~1:5, In:Ga).
Figure S2. Current-density vs. voltage plots of the three self-assembled monolayers (SAMs) of $n$-alkanethiolates that were used to calculate $\beta$. Each trace represents geometric averages from at least 100 traces of a SAM measured by contacting a ~20-µm EGaIn electrode (formed by bifurcating a drop between a film of Ag and a needle attached to a syringe) to the surface of the SAM on a thin film of Ag supported by Norland Optical Adhesive 61. The error bars represent one standard deviation from a Gaussian fit of the values of $J$ for each value of $V$. 
Figure S3. A plot of 14 $J$-$V$ traces collected at a single location on the junction Ag-$SC_{12}$/$C_{12}S$-Hg, under a solution of dodecanethiol in hexadecane. In Hg junctions, solvent molecules intercalated into the interface between the SAMs, and caused the observation of initial low-$J$ traces (the first trace shown here) before being expelled from the junction. These traces were absent in the data from EGaIn junctions. After 14 traces the junction failed, and the current quickly increased to 10 A/cm$^2$ as amalgamation is precipitated by a defect in the SAM—so-called “high-$J$ filtering”
References.