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Eutectic Gallium–Indium (EGaIn): A Moldable Liquid Metal for Electrical Characterization of Self-Assembled Monolayers**

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Herein we describe the formation of conformal electrodes from the fluid metal eutectic, Ga–In (which we abbreviate "EGaIn" and pronounce "e-gain"; 75% Ga, 25% In by weight, m.p. = 15.5°C),[1] and their use in studying charge transport across self-assembled monolayers (SAMs). Although EGaIn is a liquid at room temperature, it does not spontaneously reflow into the shape with the lowest interfacial free energy as do liquids such as Hg and H_2O: as a result, it can be formed into metastable, nonspherical structures (e.g., cones, and filaments with diameters $\geq 1\ \mu m$). This behavior, along with its high electrical conductivity ($3.4 \times 10^4\ \mathrm{S\,cm^{-1}}$)[2] and its tendency to make low contact-resistance interfaces with a variety of materials,[1] makes EGaIn useful for forming electrodes for thin-film devices.[3–5] We discuss the convenience and precision of measurements of current density (J, $\mathrm{A\,cm^{-2}}$) versus applied voltage (V, V) through SAMs of n-alkanethiolates on template-stripped, ultraflat Ag[6] ($\mathrm{Ag\text{–}SC}_n \equiv \mathrm{Ag\text{–}SC}_nH_{2n+1}$, $n = 10, 12, 14, 16$) using EGaIn.

An ideal electrode for physical-organic studies of SAMs would 1) make conformal, but nondamaging, physical contacts, 2) readily form small-area (micrometer diameter) contacts, to minimize the contribution of defects in the SAM to J, 3) form without specialized equipment, and 4) be nontoxic. Point 3 is particularly important: elimination of procedures such as evaporating metals or lithographic patterning would allow a wide range of laboratories—including those without access to clean rooms—to survey relationships between structure and electrical conductivity.

There are currently three general techniques for forming top contacts for large-area (i.e., more than a few molecules) electrical measurements on SAMs of organic molecules: 1) The direct deposition of metals such as Au or Ti by using electron-beam or thermal evaporation[7] ensures atomic-level contact, but results in low yields of devices[8] owing to damage to the organic monolayer by reaction with hot metal vapors,

and in the formation of metal filaments that short the junctions.[9] 2) The installation of an electrically conducting polymer[10,11] between the SAM and a metallic top contact inhibits formation of metal filaments, but the instability of SAMs of alkanethiolates to the temperatures[12] required to anneal most electroactive polymers limits the broad application of this approach. 3) The use of Hg allows formation of conformal contacts at room temperature,[13,14] but Hg is toxic, amalgamates with metals,[15] tends to form junctions that short, is difficult to form into small contacts, and measurements with Hg must be performed under a solvent bath.

EGaIn does not flow until it experiences a critical surface stress ($0.5\ \mathrm{N\,m^{-1}}$), at which point it yields (i.e., flows).[16] EGaIn 1) makes conformal, nondamaging contacts at room temperature, 2) can be molded into nonspherical shapes with micrometer-scale (or larger) dimensions, 3) is commercially available, 4) can be deposited with a pipette or syringe without high temperatures or vacuum, 5) has a low vapor pressure, and 6) is nontoxic. The work function of EGaIn (4.1–4.2 eV) is close to that of Hg (4.5 eV), but EGaIn does not alloy with many metals. It is therefore an ideal replacement for Hg, especially in devices that incorporate SAMs (which are generally formed on Au or Ag).

Auger spectroscopy on samples of EGaIn in air show that its surface is principally composed of oxides of Ga (see the Supporting Information); gallium oxide is an n-type semiconductor. There is undoubtedly an adsorbed film of water on this surface, as EGaIn has a high surface free energy (ca. 630 $\mathrm{dynes\,cm^{-1}}$),[2] as do oxides formed from similar metals.[17] During our measurements, there were no observable changes in the average magnitude or range of J when EGaIn was allowed to sit in air for extended periods before we deposited it on the SAM, or when we performed the measurements using the same drop of EGaIn to form between three and five junctions, or while we flowed dry N_2 over the sample: therefore the contribution of the surface oxide to J was probably constant for the duration of the experiments.

We formed EGaIn electrodes by suspending a drop of EGaIn from a metal 26s-gauge needle affixed to a 10-µL syringe, bringing the drop into contact with the bare surface of a sacrificial film of Ag using a micromanipulator, and retracting the needle slowly (ca. 50 $\mu m\,s^{-1}$); the EGaIn adhered to both the needle and the Ag (Figure 1). The drop of EGaIn pinched into to an hour-glass shape until it bifurcated into two structures, one attached to the syringe (a cone approximately 0.05 µL in volume) and one (which was discarded) attached to the Ag. We produced conical tips of EGaIn with diameters ranging from less than 1 µm to 100 µm; the larger the bore of the needle, and the more rapidly we

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Figure 1. A series of photographs of the formation of a conical tip of EGaIn. From left to right: A micromanipulator 1) brings a drop of EGaIn suspended from the needle of a syringe into contact with the bare, reflective surface of an Ag film, and 2) raises the syringe until the EGaIn separates into a conical tip (which remains attached to the needle of the syringe) and a drop on the Ag surface. The pictures are sequential and show the formation of a single tip; the time spanned by this sequence is less than 5 s.

raised the syringe, the larger the tip. The EGaIn tip protruding from the needle did not retract into a semispherical droplet (as would Hg). Using the micromanipulator, we brought the EGaIn tip into contact with a SAM (Ag–SC$_n$). Convergence of the tip with its reflection on the Ag substrate indicated contact.

We recorded J as a function of V (J–V traces; $V = -0.5 \rightarrow 0.5$ V) through these junctions. The magnitude of J decreased as the length of the alkyl chains in the SAM increased (for $|V| > 0.2$ V). This decrease was exponential for $n = 12, 14, 16$ at $V = 0.5$ V (with characteristic attenuation parameter $\beta = 0.43$ Å^{-1}), as expected for transport mediated by nonresonant tunneling.[7] Our value for β is lower than values measured through SAMs of n-alkanethiolates with other types of junctions (0.58–0.87 Å^{-1}).[13] We emphasize, however, that this work is the first measurement of current through a single-layer SAM under ambient conditions, so the comparison of β to values obtained from other methods is not straightforward. We are currently investigating the physical significance of β (and its dependence on V) for this system.

Measurements using EGaIn were much more convenient than those using Hg: To stabilize the Hg junction to applied voltage, we had to form a second SAM on the Hg electrode and immerse the entire junction in a solution of thiol in hexadecane.[13] This process took up to 10 minutes per junction, whereas the EGaIn junctions took seconds to form. When we collected data for the EGaIn junctions under ambient conditions; approximately 90% of the junctions survived 30 J–V traces (an example is shown in Figure 2a[18]), after which point we stopped acquiring data. (The other 10% shorted during the first trace.) Without a solvent bath or second SAM, 100% of the Hg junctions shorted during their formation.

The EGaIn junction (Ag–SC$_n$/EGaIn), which included two interfaces—the covalent Ag–S interface, and the noncovalent CH$_3$/EGaIn interface—is also much simpler conceptually than the Hg junction (Ag–SC$_m$//C$_n$S–Hg), which has, nominally, three interfaces: the covalent Ag–S interface, the van der Waals (//) interface between the two SAMs, and the covalent S–Hg interface.

The EGaIn system addresses one of the weaknesses of organic electronics by providing a high yield of usable
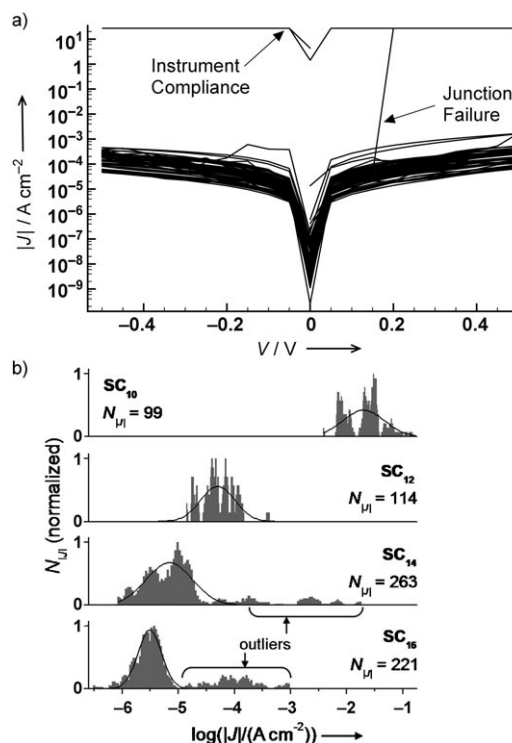

Figure 2. a) A plot of 30 J–V traces taken under ambient conditions at five different locations on the junction Ag–SC$_{12}$/EGaIn with a glass slide supporting the film of Ag. The trace that exceeds 10 A cm^{-2} represents the one junction that shorted (on the first scan at location two) when EGaIn penetrated the SAM and contacted the underlying Ag (the trace is linear before leveling off at the compliance limit of the electrometer). No junctions failed after the first scan was completed. b) Normalized histograms of log($|J|$) at $V = +0.2$ V and Gaussian fits to these histograms for SAMs of SC$_n$ ($n = 10, 12, 14, 16$) on template-stripped Ag (see Figure S1 in the Supporting Information for J–V curves for each value of n). The y axis is $N_{|J|}$, the number of times each value of J was measured, and is normalized to the highest value of $N_{|J|}$ for each SAM. All measurements were made under ambient atmosphere. One contributor to the absence of outliers in the histograms for $n = 10, 12$ is, we believe, that $N_{|J|}$ for these SAMs is approximately half of that for $n = 14, 16$. The data for parts (a) and (b) represent 100% of the traces that were completed (ca. 90% of all attempted traces); around 10% of the junctions shorted on the first trace.

junctions, and it is sufficiently convenient experimentally that it generates statistically large numbers of complete J–V traces. Figure 2b shows histograms of the values of log($|J|$) (the number of times $N_{|J|}$ we measured a value of $|J|$ versus log($|J|$) for a particular value of V) for the junctions Ag–SC$_n$/EGaIn ($n = 10, 12, 14, 16$). Each histogram—which includes 100 or more values of J measured over at least five locations on each of two independently prepared SAMs—is representative of those for all values of V. For the SAMs Ag–SC$_{10}$ and Ag–SC$_{12}$, a single Gaussian function encompassed all the data, whereas for Ag–SC$_{14}$ and Ag–SC$_{16}$, the data partitioned into a set that fit a Gaussian function of width similar to that for Ag–SC$_{10}$ and Ag–SC$_{12}$, and a set that we classify as "outliers". As we have done previously,[13] we attribute the width of the log-normal distribution of J to the contribution of defect-mediated current through the SAMs (see the

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Supporting Information). We believe that EGaIn does not introduce additional error.

Stable, nondamaging top contacts based on EGaIn will, we believe, make it possible to carry out studies relating organic structure to tunneling current in structurally defined single-layer SAMs. The ability to acquire statistically large numbers of data is a necessary step toward gathering statistics that are critical for the physical modeling of transport through ensembles of molecules that include defects. The procedures we employ to study SAMs should extend readily to the characterization of other materials that are relevant to molecular and organic electronics; we have already used EGaIn to measure charge transport through arrays of colloidal semiconductor quantum dots,[19] and are exploring its utility as an electrode for conducting polymers. The low toxicity, processability, moldability, and low reactivity of EGaIn in air also make it and related low-melting-point alloys candidates for incorporation into functional, packaged organic devices.

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[18] The origin of the sudden change in the shape of the *J*–*V* trace in Figure 2a between $V = \pm 0.05$ is probably a switch from the "low-bias regime" ($eV \ll \Phi$) to the "intermediate-bias regime" ($eV < \Phi$), whereby Φ is the height of the tunneling barrier imposed by the organic monolayer (within the often-used Simmons model). In the low-bias regime, *J* depends only linearly on *V*, but, in the intermediate bias regime, *J* depends exponentially on *V* as a result of the so-called "barrier-lowering effect" of the applied bias. We did not acquire data in small enough intervals of *V* to capture the shape of the *J*–*V* response in this region; the transition from low- to intermediate-bias regimes therefore appears as a discontinuity in the plot in Figure 2a; see: Chen et al. in *Molecular Nanoelectronics* (Eds.: M. A. Reed, T. Lee), American Scientific Publishers, Valencia, **2003**, pp. 1–76.
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