Contacting Organic Molecules by Soft Methods: Towards Molecule-Based Electronic Devices

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CONSPECTUS

Can we put organic molecules to use as electronic components? The answer to this question is to no small degree limited by the ability to contact them electrically without damaging the molecules. In this Account, we present some of the methods for contacting molecules that do not or minimally damage them and that allow formation of electronic junctions that can become compatible with electronics from the submicrometer to the macroscale. In "Linnaean" fashion, we have grouped contacting methods according to the following main criteria: (a) is a chemical bond is required between contact and molecule, and (b) is the contact "ready-made", that is, preformed, or prepared *in situ*?
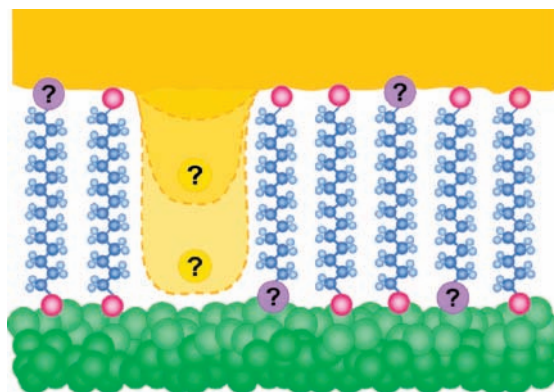
Contacting methods that, so far, seem to require a chemical bond include spin-coating a conductive polymer and transfer printing. In the latter, a metallic pattern on an elastomeric polymer is mechanically transferred to molecules with an exposed terminal group that can react chemically with the metal. These methods allow one to define structures from several tens of nanometers size upwards and to fabricate devices on flexible substrates, which is very difficult by conventional techniques. However, the requirement for bifunctionality severely restricts the type of molecules that can be used and can complicate their self-assembly into monolayers.

Methods that rely on prior formation of the contact pad are represented by two approaches: (a) use of a liquid metal as electrode (e.g., Hg, Ga, various alloys), where molecules can be adsorbed on the liquid metal and the molecularly modified drop is brought into contact with the second electrode, the molecules can be adsorbed on the second electrode and then the liquid metal brought into contact with them, or bilayers are used, with a layer on both the metal and the second electrode and (b) use of preformed metal pads from a solid substrate and subsequent pad deposition on the molecules with the help of a liquid. These methods allow formation of contacts easily and rapidly and allow many types of monolayers and metals to be analyzed. However, in their present forms such approaches are not technologically practical.

Direct *in situ* vacuum evaporation of metals has been used successfully only with bifunctional molecules because it is too invasive and damaging, in general. A more general approach is indirect vacuum evaporation, where the metal atoms and clusters, emitted from the source, reach the sample surface in an indirect line of sight, while cooled by multiple collisions with an inert gas. This method has clear technological possibilities, but more research is needed to increase deposition efficiency and find ways to characterize the molecules at the interface and to prevent metal penetration between molecules or through pinholes, also if molecules lack reactive termination groups.

This Account stresses the advantages, weak points, and possible routes for the development of contacting methods. This way it shows that there is at present no one ideal soft contacting method, whether it is because of limitations and problems inherent in each of the methods or because of insufficient understanding of the interfacial chemistry and physics. Hopefully, this Account will present the latter issue as a research challenge to its readers.

1. Introduction

The drive for finding ways to change the current electronic technologies to fulfill future needs is among the factors that fuel the increased interest in molecular electronics. In general, development of molecular electronics over the last decades is strongly "Galison"- rather than "Kuhn"-like, that is, more driven by the emergence of new tools than by new ideas. While scanning probe microscopies and advanced nanofabrication methods have the highest visibility among these tools, they also include advances in syntheses of relevant molecules, molecular modification of electronic materials, and ways to make electrical contacts to molecules.[1] In this Account, we focus on the last of these tools, while noting that results from research on all these methods fuel expectations to make organic molecules active components in future electronics.

Making electrical contacts to solids is often a combination of science, technology, and art, with the weight of each depending on how far technology and understanding have advanced. It is, therefore, not surprising that contacting molecules to measure electronic transport through them by connecting them to the macroscopic world severely limits and hinders reliable and reproducible studies, as well as realization of molecular devices. This is due mostly to difficulties in (I) attaching the molecules reproducibly to the electrodes, needed to perform systematic studies, because, for general laboratory use, one wants the method not to be limited to specific types of molecules, while, for practical use, quite different requirements may dominate, and (II) understanding how electrodes and molecules interact. Such understanding is critical for knowing how details of contacting, in terms of materials and methods, affect the resulting molecule-based device characteristics.

Several experiments show substantial changes in the conductivity of conjugated "molecular-wire" molecules by changing the type or geometry of their contacts to surfaces.[2] Experimental conductivity values can differ by orders of magnitude for the same molecule,[2] something that makes even those cases, where some agreement is obtained with values obtained from theoretical models, of limited value. In this Account, we review methods for contacting molecules to form electronic junctions of sizes well beyond a few hundreds of molecules, that is, junctions for micro- to macroelectronics. We group the methods, roughly, according to the following criteria: (i) whether a chemical bond is required between contact and molecule (see section 2) or (ii) whether the contact is pre-

formed, "ready-made" (see section 3), or is prepared *in situ* (mostly by evaporation; see section 4).

By focusing on contacts to many molecules, observed effects will be averaged over all the molecules.[2] As a result, we lose single-molecule effects but can gain in reproducibility. In addition such contacts are more likely to be relevant for possible future devices. Approaches for contacting isolated single molecules or isolated small ensembles (mostly <100) of molecules, such as nanoparticle-coupled conducting atomic force microscopy (AFM),[3] direct conducting AFM,[4] electroless deposition,[5] mechanically controllable break junction,[6] bridging nanoparticles,[7] and electromigration,[8] are outside the scope of this Account. A more comprehensive overview that includes also those approaches and others (e.g., crossed wires,[9] conductive polymer spin-coating,[10] soft contact lamination[11]) will be presented elsewhere.

2. Chemical-Bond-Limited Approach

While all methods that use the chemical bond approach are limited by the choice of molecules and of molecule/contact combinations, reproducibility of the resulting device structure and of the transport measurements performed on them is often better with than without a chemical bond between molecule and contact.

2.1. Transfer Printing. Complete, "ready-made" features can be transferred onto substrates without the need for energetic photon, ion, or electron beams.[11,12] In transfer printing, a thin metal film is evaporated onto an elastomeric stamp (e.g., polydimethylsiloxane, PDMS) and electrical contacts are made by mechanically contacting the metal-coated PDMS stamp and the organic layer. Nanometer-sized features and devices fabricated on flexible substrates have been demonstrated.[11]

The weak point of the method is the transfer of the metal by mere mechanical contact because, in principle, there is no driving force for such transfer. This problem can be overcome by using molecules that form chemical bonds with the "to-be-transferred" metal pad (see ref 11 and references therein). Figure 1 illustrates this process for fabricating top metal electrodes to form metal/molecule/substrate junctions.

A variety of materials, surfaces, and chemical systems of interest can be used with the (nano)transfer printing approach. The chemical systems generated by transfer printing, TP, are not damaged by the tools used to create them and can, thus, be integrated easily into systems where tools such as energetic beams would be too destructive. In particular, these methods found use for patterning monolayers. (Photo)electri-
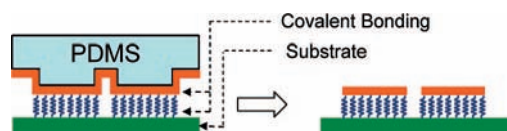
FIGURE 1. Schematic illustration of (nano)transfer printing, (n)TP. A substrate covered by a monolayer of molecules with an exposed reactive terminal group (e.g., thiol) is mechanically contacted by the metal-coated elastomeric PDMS. The stamp is removed from the substrate, and the pattern is left on the molecules because metal adhesion to PDMS is weaker than that to the exposed thiol group.
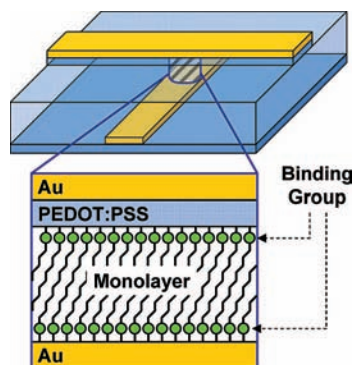

FIGURE 2. Schematic illustration of a patterned molecular junction made by spin coating a conductive polymer of poly(3,4-ethylenedioxythiophene) stabilized with poly(4-styrenesulphonic acid) (PEDOT/PSS).

cal measurements show that direct contacts between the transferred metal and substrate electrodes are reduced in TP diodes, compared with devices made by vacuum metal evaporation onto the molecular layer. The ability to define nanometer-scale structures, in which case the method is called nanoTP, nTP, and to fabricate devices on flexible substrates, both of which are very difficult to achieve by conventional techniques, is an additional advantage. The recent results of Guerin et al., showed relatively poor reproducibility, small effective contact area and rather mediocre electrical characteristics for devices prepared by nTP on molecules without the chemical binding group to the metal, stressing the need for bifunctional molecules.[13] Yet, making monolayers with bifunctionalized molecules, such as dithiols, is not trivial, because, for example, if too long (and too flexible) a molecule is used, both thiol groups can bind to the substrate.[14]

2.2. Spin Coating of Conductive Polymer. Metal/molecular insulator/organic conductor/metal junctions, up to 100 μm in diameter with close to 100% yield and a shelf life of over several months were made with this approach (see Figure 2).[15,16] The keys to producing these junctions were use of a conducting polymer layer sandwiched between a thiol-terminated monolayer and the top electrode to prevent electrical shorts and processing within lithographically defined
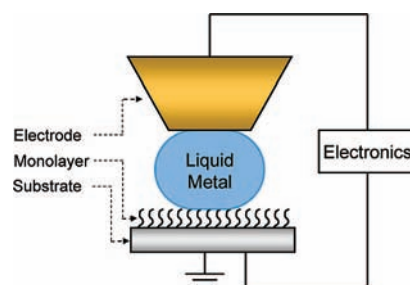

FIGURE 3. Schematic illustration (not to scale) of a molecular junction that is formed with a liquid metal contact.

vertical interconnects (or via holes) to prevent both parasitic currents and interaction between the environment and the monolayer.

The technique appears simple, is compatible with standard integrated circuit fabrication processes, and can be scaled up. It will be interesting to see how well this approach works with molecules that cannot bind chemically to the polymer.

3. "Ready-Made" Approaches

3.1. Liquid Metal. A simple way for nondestructive contacting of organic molecules is to use a liquid metal as electrode (Hg is the obvious and most common choice). Molecules can be adsorbed on the liquid metal and the molecularly modified drop is brought into contact with the second electrode or molecules can be adsorbed on the second electrode and the liquid metal brought into contact with them (Figure 3); see refs 17–22 and references therein.

For Hg/monolayer/metal junctions, the breakdown voltages and tunneling characteristics of alkanethiols and polyphenylenes were characterized.[20] A feature of these junctions (and those formed by lift-off; see section 3.2) is that both single and double monolayers, that is, bilayers, can be prepared and studied. Thus, a bilayer can be formed, using two Hg drops, each with an adsorbed monolayer or by having a monolayer on both the Hg and the substrate.[20] Using this (Hg/monolayer//monolayer/Hg) approach, Holmlin et al.[23] found that by changing the interaction from covalent to hydrogen or van der Waals-like bonds, conductivity changed by more than 4 orders of magnitude. Junctions of mixed monolayers that display rectification were formed with tetracyanoquinodimethane-functionalized decyldisulfide.[24]

Hg contacts to alkyl-chain monolayers on n- or p-Si[25] and -GaAs[26,27] provided a reproducible way to form junctions (at >50%, at times 80% yield) with reproducible transport results. Using a semiconductor rather than a metal as one of the contacts has some interesting consequences. With n-type semiconductors, the Hg contact to the molecular monolayer

covered semiconductor was rectifying, with thermionic emission dominating transport at low and tunneling at higher forward bias. The thermionic emission transport characteristics were found to be more sensitive to monolayer and junction quality than any other physical measurements. At higher forward bias the n-type systems behaved rather similarly to metal/molecule/metal ones. With p-type substrates, tunneling dominated over most of the bias voltage range. Because of the reproducibility of the data, provided by the Hg contact, the transport characteristics could be analyzed reliably in both regimes, using the thermionic emission and the direct tunneling models. As a result, a fuller description is possible than for metal/molecule/metal junctions. Such analyses led to the realization that hybridized orbital (valence band (VB) and conduction band (CB) levels that hybridize with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) ones of the molecules) "induced interface states" need to be included in tunneling transport descriptions.

Comparing the Si and GaAs systems showed that here the substrate has an important role in transport, for example, by changing the relative importance of tunneling vs thermionic emission. Remarkably, adding a Hg—S chemical bond at the Hg interface for the Si systems did not change the tunneling transport efficiency, in contrast to other experimental results where such an extra bond does make a difference.[2,28] In this case, a combination of photoemission data and electronic structure computations showed that the orbitals involved in bonding (and antibonding) are significantly farther from the Fermi level than the above-mentioned induced interface states.

For GaAs, changing the chemical bond to the semiconductor (S-terminated alkyl to As or phosphonate-terminated alkyl to Ga) did affect transport, an effect that was expressed by a difference in the effective electron mass for tunneling, due to the change in interface energetics and potential profile between the two systems.

These results are noted here because at present only a few contacting methods appear capable of yielding sufficiently robust and reproducible experimental results to allow studies like these. Indeed, the difficulty to obtain reproducible results was one of the main driving forces for researchers to use "conductance histograms" to measure single-molecule conductance.[29,30]

With cyclic disulfide molecules adsorbed on a Hg drop and brought in contact with a SiO_x-on-Si substrate, reproducible, stable negative differential resistance (NDR) at room temperature was found, the result of reversible changes in the molecule—Hg electrode contact.[22]
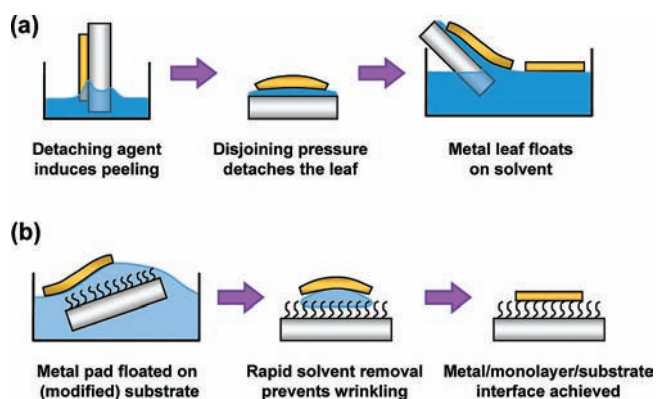

FIGURE 4. Schematic description of the lift-off, float-on (LOFO) procedure: (a) lift-off of evaporated leaf from a glass slide using a detaching agent; (b) float-on of the leaf on the solid substrate in a liquid medium.

While liquid metal electrodes will not or rarely have practical technological use, they can be formed fast, are easy to construct, and allow multiple monolayer and metal variations to be analyzed. The method is limited to ensemble measurements and cannot be performed below the metal freezing point. Also, it is as yet unclear whether there are cases where the liquid metal contact can introduce defects in or cause reconstruction of the monolayers because of hydrostatic pressure.[20]

3.2. Lift-Off-Assisted Approaches. These methods rely on capillary interactions, induced by the liquid–solid interfaces between two solids and a common liquid for transferring thin solid metal films onto (molecularly modified) solid substrates. The first method of this type, termed lift-off, float-on (LOFO), was developed by Vilan et al.[31] and is compatible with molecular adsorption either on the substrate, on the transferred solid film, or on both solids, with no discernible degradation of the monolayer.[31] The general procedure includes two major steps (see Figure 4).

Several device types were made with LOFO. Among these, we note metal/GaAs[32,33] and metal/ZnO[34] junctions. Systematic studies of electronic transport across these junctions showed them to be unequivocally controlled by a discontinuous partial monolayer of polar molecules with average organization because they always had the same group bound to the surface. Because electron transport through the molecules seemed to contribute little or nothing to the change in junction properties, the observed findings were attributed entirely to a change in effective electron affinity of the modified surface. Such changes result from electrostatic effects, due to the average dipolar layer formed by the molecules.

A complementary configuration, using Si—(SiO_x)—Au diodes with polar molecules adsorbed on the Au contacts, was also

probed.[35] In such diodes, the metal work function, rather than the semiconductor's electron affinity was changed. In this case, there was also some contribution from tunneling across the molecules because of the higher density and better organization of the molecular film on Au than on GaAs. In all cases, the observed differences between diodes were explained well by differences in molecular dipoles due to the change in molecular dipoles. In contrast to vacuum evaporation (see section 4) with LOFO, any metal diffusion through small (1–2 nm) pinholes in the organic monolayer is extremely unlikely. At the same time, though, the area of the molecules contacted with LOFO is smaller than that with evaporated contacts. A possible reason is that etching the glass/metal pad during the lift-off process leaves a relatively rough surface (>1 nm).[31,33]

Melosh and co-workers further developed the method using a polymer to transfer a top metal contact onto molecular films without macroscopic distortion or damage.[36] The key component was a hydrophobic polymer backing layer on preformed electrodes. Such backing provides mechanical stability and a thermodynamic driving force to eliminate wrinkling of the pads, a problem with LOFO. With this technique, termed PALO (polymer-assisted lift-off), metal-electrode devices were fabricated in parallel over a wide range of electrode dimensions (10^{-4} to 9 mm^2; LOFO areas were limited to ~0.1 mm^2) with lithographically defined spatial registry. As in the case of LOFO, only very few (here <10%) of the molecular junctions were short-circuited.

LOFO and PALO can be viewed as macroscopic complements to chemisorption of metallic nanoparticles on suitably terminated monolayers,[3] but with wider use, since they do not rely on actual chemical bonding to the metal. Because in LOFO and PALO the surfaces that are to be bonded are kept wet until the very moment of establishing the electrical contact and contact formation occurs at (or very close to) room temperature, the methods are also suitable for electronic devices incorporating biological molecules.[37] Such materials commonly suffer severe rearrangement when removed from their original environment. It will be interesting to apply LOFO and PALO to Langmuir–Blodgett films by floating the contacts on the molecular films directly inside the trough.

4. *In-Situ* Approach–Metal Evaporation

Vacuum deposition of metals by evaporation is one of the most common electrical contacting methods in laboratories and industry. Because the method is well-developed, its use for molecules is of great interest. The usual way of metal evaporation is described first, followed by an adaptation that appears more suitable for contacting molecules.

4.1. Direct Evaporation. Making electrical contacts by metal evaporation relies on vaporizing the metal by heating it to sufficiently high temperatures and then recondensing the vapor onto a cooler substrate. Normally, the metal atoms and clusters reach the substrate with high temperatures and kinetic energies. This, together with radiation emitted from the heated source, can modify the substrate surface, and molecules on the surface can be damaged. Also the metal can penetrate through the molecules to the substrate,[38] *even if the sample is cooled during metal evaporation.*[39]

Several studies have analyzed the interaction between the evaporated atoms and clusters and organic molecules. If the molecules' terminal groups react with the impinging metal, this can control somewhat the damage and decrease diffusion of metal through the molecules.[38,40–42] The balance between nucleation on top of the monolayer and diffusion through the layer depends critically on the functionality of the terminal groups and the type of the incoming metal atoms. If the metal atoms have low reactivity toward the terminal groups, they can penetrate through the organic monolayer toward the counter electrode and, eventually, form an adlayer between the electrode and the monolayer. Such a process can produce metallic "columns" that connect the upper and lower contacts to each other. If the bottom electrode, on which the molecules are adsorbed, is metal, these columns may short the device. If the metal easily oxidizes (e.g., Al), then, because the columns are very thin, instead of shorts, well-defined relatively insulating pillars can form. The height of these pillars will be determined by the molecular layer's width. Thus, electrical transport measurements for metal/molecular layer/metal junctions may reflect transport through the pillars, if those are more conductive than the molecules, rather than through the molecules. Still, the experimenter may be misled in viewing the results as evidence for transport through the molecules while, in reality, the molecules only function as spacers that determine the width of the medium through which the electrons pass.

If the impinging metal reacts readily with the molecular terminal group, the metal will remain on the top of the monolayer by forming bonds with its end groups.[38,41,43] The higher the reactivity of the terminal groups is with the metal, the more likely it is that the metal remains on top of the monolayer, bound to the molecules' end groups, the less likely is metal interdiffusion through the monolayer,[38,41] and the shorter molecules can be used.[44] Indeed, a three carbon atom chain with a thiol end group was reported to block Au diffu-

sion to the substrate.[44] It is not yet clear how thiol terminations can prevent metal diffusion through 2D pinholes that may exist, especially in layers of short molecules.[45]

In view of the above, it is fair to state that *vacuum* deposition of metals as used in microelectronics today is too harsh a method for most organic molecules or is limited to a narrow range of organic molecules that, basically, have reactive, sacrificial terminal groups and that will be altered by reaction with the metal. Even experiments that use cooled substrates should be viewed with caution, also if they do not show obvious device shorting.[46,39] Rather, unless evidence to the contrary is available, it is likely that the measured electrical characteristics represent an average of transport across damaged and undamaged molecules and of parts that are and are not shorted.[39] Other criteria need to be used to judge if damage resulted from contact deposition (see section 4.2).

4.2. Indirect Evaporation. Evaporation of metals under conditions that minimize exposure of the substrate to high energies and temperatures can significantly limit damage to the molecules. One way to accomplish this is to partially backfill the evaporator chamber with an inert gas. In this way, the metal atoms and clusters that reach the sample surface will be cooled by multiple collisions with the inert gas, a process that can be aided further by turning the sample away from the source. Naturally these measures have a price, a drastic reduction (up to $100\times$) in deposition rates of the metal atoms or clusters on top of the samples, which will range between 10^{-4} to 10^{-2} nm/s.[39] By using e-beam instead of thermal evaporation, deposition is mainly of atoms, with only a minor fraction of clusters, making the process better controllable with a smoother surface of the evaporated film. Turning the sample away from the source also reduces sample heating by avoiding direct irradiation of the sample (see Figure 5).[39,47] Naturally, also cooling the sample is useful to limit sample heating, but the cooled sample should not be the coldest place in the evaporation chamber to avoid condensation of residues onto the sample. Therefore, a second coldfinger, colder than the sample should be present in the chamber (see Figure 5).

Due to the difficulties to characterize molecules at the substrate/metal interface and to extract information on the state of the molecules from the junction's electrical behavior, we developed a different approach to assess damage to the molecules, after metal evaporation onto them, building on our earlier work on semiconductor surface modification by molecular dipoles,[32,39] reviewed in a previous Account.[48] Adsorbing a series of molecules with systematically varying dipole moments onto a semiconductor leads to a systematic variation in the electron affinity of the modified semiconductor sur-
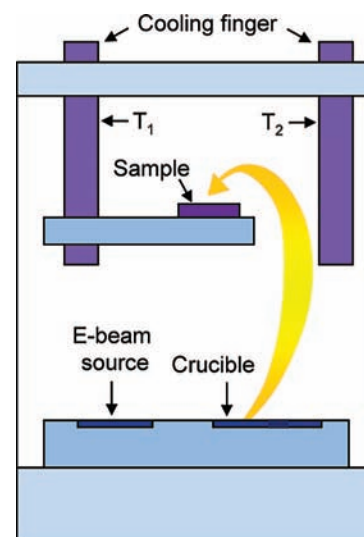

FIGURE 5. Schematic view of indirect cooled evaporation. Samples are placed on a holder and hidden from the crucible. The difference from direct evaporation is that there the samples "see" the metal crucible and evaporation itself occurs at the base vacuum pressure without the presence of inert gas. The second cold finger assures that the sample will not be the coldest spot in the chamber to avoid condensation of spurious residues on it; that is, in the figure $T_2 < T_1$.

face. If a metal contact is deposited on that surface without damaging the molecules, then the Schottky barrier height for electron transport across the resulting metal/(molecules on semiconductor) junctions should show a similar systematic change.

We used molecules with the same binding group to the semiconductor surface and with a terminal group exposed to the outside and, thus, to the deposited metal, so as to change the molecule's dipole moment. Thus yields a very sensitive tool to assess the effect of deposition damage on the molecules. Indeed, we find that details of the evaporation process can completely change the resulting device characteristics. "Indirect" evaporation is found to cause far less damage than "direct" evaporation, even with a cooled sample, yielding reproducible results, especially if Pd is used for contacting.

Comparing molecular effects on metal/molecular layer/GaAs junctions prepared by indirect evaporation and by other soft contacting methods showed that Au is not an optimal choice as evaporated contact metal. The reason is the ease by which Au (as well as Ag) can diffuse between molecules, something that can lead, apart from direct contact−substrate connections, to undesired and uncontrollable interfacial interactions. Such diffusion is mostly absent with Pd, which grows preferably by a 2D mechanism, which limits the metal's interaction with the molecules.[39]

5. Summary and Outlook

While the properties of molecules play a significant role in the characteristics of molecular devices, the nature of the electrical contact to the molecules can dictate the overall behavior of the device. Subtle differences in contacting to form the molecular junction can change the device characteristics. A complication with molecular junctions is the difficulty to know the chemical nature and structure of the contacts. The need to use contacts that are (at least) several tens of nanometers thick (or in diameter, for contact by metallic nanoparticles) or to get continuous metal films as electrical contacts makes characterization of the molecules below the contacts by normal surface analyses difficult, although there are reports on infrared spectroscopy of molecular organic layers buried under a thin metal film.[49,50]

For single molecules and small ensembles of molecules, systems not considered in this Account, inelastic electron tunneling spectroscopy (IETS) was used to get vibrational spectra of the molecules buried under a metal contact.[44,51–53] With larger ensembles of molecules, ballistic energy electron microscopy may, in some cases, help to characterize buried molecular films.[54,55] It is clear, though, that it will be of very great interest to find ways of functional imaging of buried molecules.

To summarize and provide a perspective for the future, we note that among the various approaches and architectures that have been used to contact organic molecules, at present very few have a proven track-record for high yield and reproducibility to allow performance of systematic studies. There are advantages and disadvantages to each contacting approach, and the choice will be determined by weighing each method's (dis)advantages. Methods requiring a chemical bond seriously limit the choice of molecules and of molecule/contact combinations but can improve resulting device structure and fabrication and measurement reproducibility. Liquid metals, while likely not practical technologically, form contacts easily and rapidly and allow multiple monolayer and metal variations to be analyzed. The method is limited to ensemble measurements and cannot be performed below the metal freezing point. Indirect vacuum evaporation of metals has clear technological possibilities, but more research is needed to ensure that metal penetration between molecules or through pinholes can be prevented, if molecules lack reactive termination groups, to increase deposition efficiency and to find ways to characterize molecules at the interface.

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FOOTNOTES

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