

Molecular control over Au/GaAs diodes

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The use of molecules to control electron transport is an interesting possibility, not least because of the anticipated role of molecules in future electronic devices¹. But physical implementations using discrete molecules are neither conceptually^{2,3} simple nor technically straightforward (difficulties arise in connecting the molecules to the macroscopic environment). But the use of molecules in electronic devices is not limited to single molecules, molecular wires or bulk material. Here we demonstrate that molecules can control the electrical characteristics of conventional metal–semiconductor junctions, apparently without the need for electrons to be transferred onto and through the molecules. We modify diodes by adsorbing small molecules onto single crystals of n-type GaAs semiconductor. Gold contacts were deposited onto the modified surface, using a ‘soft’ method to avoid damaging the molecules⁴. By using a series of multifunctional molecules whose dipole is varied systematically, we produce diodes with an effective barrier height that is tuned by the molecule’s dipole moment. These barrier heights correlate well with the change in work function of the GaAs surface after molecular modification. This behaviour is consistent with that of unmodified metal–semiconductor diodes, in which the barrier height can depend on the metal’s work function.

The lack of clear understanding of electron transport involving non-conjugated molecules⁵ contrasts sharply with the rather detailed understanding of transport in solids with extended bonding (non-molecular ones), also on a mesoscopic scale. Most work in this area is concerned with electron transport through molecules^{6,7}, and several mechanisms have been proposed for such transport⁸.

The experiments reported here are based on our ability to use series of molecules for systematic modification of the surface electronic properties of semiconductors and metals^{9–14}. In terms of actual electron transport, we used such molecules to explore molecular control over CuInSe₂/CdS (ref. 15) and CdTe/Au (ref. 16) diode characteristics. Characteristics of organic LEDs were changed by adsorption of nitrobenzoic acid and a carboxylated Ru dye¹⁷, or of thiols with two different dipoles¹⁸. Krueger *et al.* showed¹⁹ that the current–voltage (*I*–*V*) characteristics of diodes (made by spin-coating an organic hole conductor on thin polycrystalline TiO₂ films), onto which a series of benzoic acids was adsorbed, change with the dipole moments of the benzoic acid used.

A significant problem in all such studies is deposition of the second contact on the molecularly modified surface^{20,21}. Techniques used to make ordinary types of diodes, such as sputtering and vacuum evaporation, can (and often will) damage the molecules and/or change the surface in an uncontrollable fashion (see ref. 4 for a review of the various methods tried for contact deposition on organic molecular monolayers). The encouraging preliminary results obtained for less common types of diodes, made with milder methods (for example, electrodeposition of CdS onto molecularly modified CuInSe₂; ref. 15) led us to search for ways to modify a more usual type of diode with molecules. Thus, we looked for single-crystal semiconductor–metal junctions to which the metal contact can be applied as gently as possible.

We used the series of tartaric acid derivatives, whose adsorption characteristics to GaAs(100) we characterized earlier. The molecules bind strongly to GaAs (pK = 4–6) via a dicarboxylic acid group¹³. A substituted benzene group is attached to the binding group, which

allows systematic modification of the molecule’s dipole (Fig. 1, inset). The molecules self-assemble onto the surface into roughly one monolayer by overnight adsorption in a 2.5 mM acetonitrile solution onto etched¹⁰ n-GaAs(100)^{13,14}. Indication of surface coverage comes from saturation of both spectroscopic (Fourier transform infrared) and electrical (surface resistance) signals. Fitting to a Langmuir isotherm shows a continuous fit over the complete range of concentration and time¹³. Hence, multilayer adsorption is very unlikely. From contact potential difference (CPD) measurements (see below), the coverage is found to be at least 2/3 of a monolayer, in accordance with results for related molecules, on Au (ref. 9). Wafers were purchased from AXT Co., and Si-doped to ~10¹⁸ cm⁻³. Use of relatively highly doped GaAs assured reproducible preparation of good ohmic back contacts. The strong chemisorption of the molecules stabilizes the GaAs surface that is otherwise notoriously difficult to control. Hence, experiments with molecularly modified surfaces can be done at ambient conditions¹⁰.

Gold contacts were deposited on the modified surface in a very ‘soft’ manner. For this we adapted the ‘lift-off, float-on’ technique (LOFO)²⁰—used, for example, to prepare samples for transmission electron microscopy and to deposit epitaxial GaAs films on foreign substrates²²—for use with organic solvents instead of water. Au dots, 60 nm thick and 0.5 mm in diameter, were evaporated onto clean glass slides, from which they were allowed to peel by dipping the slide at an angle in 5 vol.% solution of HF in acetonitrile. The solvent was then changed to pure acetonitrile, which contains the modified GaAs crystal; 0.5–1 vol.% water is added to increase the surface tension, to allow the Au leaves to float. The GaAs is then lifted with the Au on top, and the samples are dried at 60–70 °C in a vacuum oven. The morphology of the contacts (at micrometre resolution) depends strongly on the floating solvent; in general, the more hydrophobic the chemisorbed molecules, the smoother the contacts. Ohmic back contact to the GaAs was made by rubbing InGa eutectic onto it. Current–voltage (*I*–*V*) characteristics were measured using a W needle, connected to a micromanipulator to

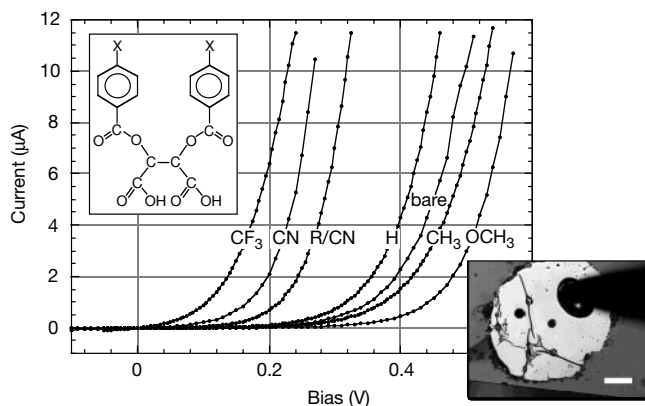


Figure 1 Characteristics of Au/molecule-on-n-GaAs junctions. Main figure, the different current–voltage (*I*–*V*) curves refer to junctions that are identical except for the substituent on the benzene ring (shown next to each curve) of the dicarboxylic acid derivatives (see inset) that were chemisorbed onto the n-GaAs surface. Each curve is typical for several measurements. No breakdown of devices was observed up to 40 mA cm⁻² and 1 V forward bias; at current densities >5 mA cm⁻², *n* increased to 5–7. The ‘bare’ curve is for a reference sample that was immersed in pure solvent, without adsorbed molecules. Because it was exposed to air after LOFO contacting, this is an oxidized surface¹⁰ without molecules. Top left inset, general chemical formulae for the molecules, chemisorbed on GaAs. The substituent, X, appears explicitly next to each curve in the main panel; R/CN is a unique ligand with asymmetric arms, one of which is a CN-substituted benzene ring, while the other is a C₁₅ alkyl chain instead of a benzene ring (compare ref. 12). Bottom right inset, optical micrograph (scale bar, 100 μm) of Au pad²⁰, floated on molecularly modified (X = CF₃) GaAs. The needle and the InGa drop (see text) can be seen on the pad (upper right corner of insert).

contact the Au dot (an InGa drop on the Au minimizes mechanical (pressure) damage to the film), and an HP 4155 semiconductor parameter analyser, in the voltage scan mode; these measurements were made mostly at ambient conditions.

I - V curves for a series of molecularly modified Au/n-GaAs junctions are shown in Fig. 1. They show qualitatively that the organic monolayer increases the current if the dipole is positive ($-\text{CF}_3$ and $-\text{CN}$ substituents), and decreases the current for negative dipoles ($-\text{CH}_3$ and $-\text{OCH}_3$), compared to the unmodified junction. Hence, a monolayer that is not providing perfect coverage of the surface (that is, with a high probability of pinholes)—made up of molecules, themselves expected to be poor electrical conductors, and so thin that electron tunnelling through them is relatively easy—tunes the diode current.

To understand this, we note that the junction's barrier height (ϕ_b), is influenced by the interface dipole (μ) at the GaAs–Au contact. In an ideal Schottky junction, the barrier height is the difference between the metal work function ($q\phi_{\text{metal}}$, with q the absolute value of the electron charge in coulombs) and the semiconductor electron affinity (χ_{sc}). The work function is a characteristic of the surface of the material, which changes with changes in the surface dipole^{23,24}. We can view χ_{sc} as the sum of a constant (χ_{sc}^0) and a dipole ($q\phi_{\text{dipole}}$) contribution. Therefore, the net barrier height is:

$$q\phi_b = q\phi_{\text{metal}} - (\chi_{\text{sc}}^0 + q\phi_{\text{dipole}}) \quad (1)$$

Here ϕ_{dipole} is the potential step due to interface dipoles²²:

$$\phi_{\text{dipole}} = \frac{N\mu \cos \theta}{\epsilon \epsilon_0} \quad (2)$$

where μ is the dipole moment (in units of C m), N is the surface density of dipoles (in m^{-2}), tilted at an (average) angle θ , ϵ is the layer's dielectric constant, and ϵ_0 is the dielectric permittivity of vacuum.

A dipole at the interface between a semiconductor and a conductor will induce or change the space charge, and thus the electric potential difference between the conductor and the bulk of the semiconductor^{23–25} (that is, the junction's barrier height, compare Fig. 8.9 in ref. 26). This is in marked contrast to what happens on a free surface, where only net surface charge, associated with surface states, can bring about such potential difference between the semiconductor surface and bulk. In the case of an interface, the effect will be there even in the absence of interface states. Such effects are expected with unintentional surface dipoles (for example, those due to surface reconstruction or to chemical metal–semiconductor interaction) and with intentionally applied ones. Experimentally, the effect of interface dipoles has been found, for example, in heterojunctions by variation of the doping at the interface²⁷. Based on this, we can expect the molecules to have a similar effect. To verify this, we fitted the I - V characteristics to the Schottky thermionic emission formula, also often used as an empirical way to describe current transport across a barrier^{23,26}:

$$I = I_s \exp\left(\frac{qV}{nkT}\right) \left(1 - \exp\left(-\frac{qV}{kT}\right)\right) \quad (3)$$

Here V is the applied bias voltage (in V), I the measured current (in A), k and T are the temperature and Boltzmann's constant, respectively, and n is the so-called ideality factor which corrects for deviation from ideal thermionic emission behaviour. I_s is the saturation current given by:

$$I_s = \sigma A^* T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \quad (4)$$

where ϕ_b is now the effective barrier height (in V); A^* is the Richardson constant (in $\text{A cm}^{-2} \text{K}^{-2}$) and σ is the contact area (in cm^2)²⁸.

We note that n can be extracted from the slope of $(\ln I) - V$ plots, and the ϕ_b can be calculated from the intercept of $\ln I$ at zero bias; for our data, n was in the range 1.3–2.3 which means that the transport mechanism is not solely one of thermionic emission^{23,26,28}. Advanced analyses could consider additional mechanisms for carrier transport across the molecularly modified interface: for example, via tunnelling (across the space charge, oxidized surface and molecular layers). Because metal–semiconductor junctions are majority carrier devices²⁹, in these Au/n-GaAs structures the carriers are expected to be primarily electrons.

The barrier height obtained here is an effective one, ignoring barrier lowering due to the GaAs surface layer, image forces²⁸, and

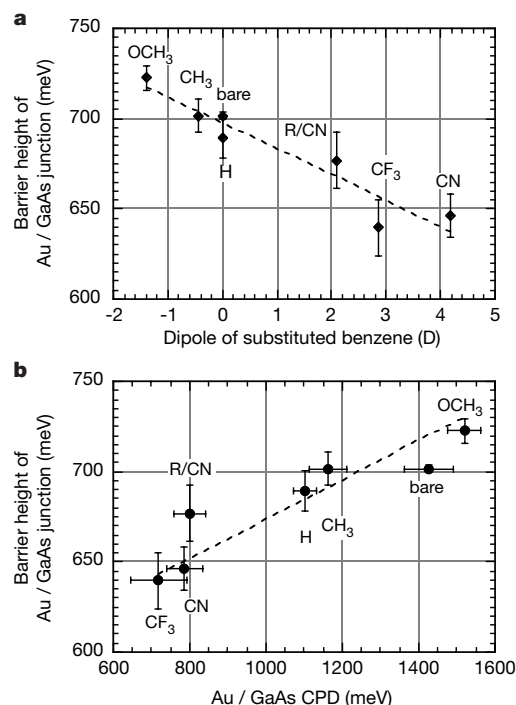


Figure 2 Dependence of the effective barrier height (ϕ_b) at the Au/derivatized n-GaAs interface on the following parameters. **a**, The dipole moment; **b**, the contact potential difference (CPD) between Au and derivatized n-GaAs surfaces. Values of the effective barrier height were extracted from I - V curves (compare Fig. 1), using equations (3) and (4). For each ligand, several samples were measured, on each of which two to four different contact pads were used, with about three measurements per pad. No significant changes were seen between 6–10 successive measurements. The error bars in the plot are the standard deviations of the measured data. We used only those curves that gave a good fit to the modified diode equation²⁸:

$$\ln\left[\frac{I}{1 - e^{-\frac{qV}{kT}}}\right] = \ln(\sigma A^* T^2) + \frac{q}{kT} \left(-\phi_b + \frac{V}{n}\right)$$

That is, we used only curves that met the requirement of continuity around zero bias, up to a negative bias of 0.1 V. On a semi-log plot (not shown), the curves are linear from -0.1 to about $+0.5$ V. The dipole moment refers to the substituted benzene part of the dicarboxylic acid^{9,12,32}. Note that the dipole of the substituted benzene moiety and the complete molecule are not identical, as the molecular dipole is the sum of those of the benzene moiety, the binding group, and the Ga–O bond. This issue is discussed in detail in refs 9 and 12. The direction of the dipole is taken as positive for the negative pole directed away from the semiconductor bulk. In **b**, the CPD was measured experimentally in an inert atmosphere using the Kelvin probe technique. The semiconductor's electron affinity, rather than its work function, was measured by using saturation illumination, that is, under conditions that minimize free surface band bending. The calculated ϕ_b value is smaller than expected without an organic layer (bare, oxidized surface), and larger than expected with the C₁₅ alkyl chain (R/CN ligand). These deviations may be ascribed to corresponding changes in the thickness and permittivity of the insulating layer²⁸, something that is being investigated further.

inhomogeneity of the barrier (compare Ch. 3 in ref. 23). The values are obtained using the nominal contact area ($\sigma = 0.002 \text{ cm}^2$) and the published²⁹ value for the Richardson factor ($A^* = 4 \text{ A cm}^{-2} \text{ K}^{-2}$). Thus, in this first approximation we neglect any (possible) effect of the molecules on the pre-exponential factor in equation (4), and attribute all of the molecular effect to the effective barrier height.

Values of ϕ_b of the molecularly modified Au/GaAs junction, extracted from the data shown in Fig. 1, using equations (3) and (4), are shown in Fig. 2a, as a function of the dipole moment of the substituted benzene group. As predicted from equations (1) and (2), the more positive the dipole, the higher the work function of GaAs, and the smaller ϕ_b .

An alternative way to measure the molecular effect on surface electronic properties is determination of the contact potential difference (CPD) between the GaAs surface and Au. We did this using a so-called Kelvin probe^{9,18,24}, which does not require physical contact with the modified surface. GaAs sample preparation was essentially the same as that used for preparing junctions. Figure 2b shows a comparison between ϕ_b of the modified Au/GaAs junction (on the y axis) and the CPD between Au and the modified 'free' GaAs surface (on the x axis).

Only 10% of the changes in CPD are expressed in the junctions' effective barrier heights. The reason is that, as written, equation (1) holds only rarely. Most semiconductors show appreciable band bending at their free surface, due to intrinsic surface states. If the density of these states is very high then they, rather than the difference in work function with the contact material, will dictate the junction's ϕ_b . This is the so-called Bardeen limit, in contrast to the Schottky–Mott limit expressed by equation (1) (refs 23, 28). In general, the less ionic the semiconductor, the less Schottky-like and the more Bardeen-like it behaves. Kurtin *et al.* defined an index of interface behaviour, S , which expresses the percentage of the work function difference that will be reflected in the barrier height³⁰. For GaAs, $S \approx 0.1$, which fits the 10% relative effect of the change in work function on ϕ_b found here.

We have shown that adsorbed molecular monolayers can tune the effective barrier height at the Au/GaAs interface, by their dipole effect. We note that such dipole effects will have to be considered when interpreting data from electron transport measurements, involving semiconductor/molecule interfaces³¹. Our results also suggest that we can tune the properties of electronic devices by way of molecular dipoles, rather than by actual electron transport through the molecules. Such an approach would allow the use of imperfect, practical molecular monolayers—with relatively easy connection to the outside world—which might fit the forecast of a future molecular central processing unit operating by electrostatic interactions rather than electron currents³. □

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Sintering dense nanocrystalline ceramics without final-stage grain growth

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Sintering is the process whereby interparticle pores in a granular material are eliminated by atomic diffusion driven by capillary forces. It is the preferred manufacturing method for industrial ceramics. The observation of Burke and Coble^{1,2} that certain crystalline granular solids could gain full density and translucency by solid-state sintering was an important milestone for modern technical ceramics. But these final-stage sintering processes are always accompanied by rapid grain growth^{3–6}, because the capillary driving forces for sintering (involving surfaces) and grain growth (involving grain boundaries) are comparable in magnitude, both being proportional to the reciprocal grain size.