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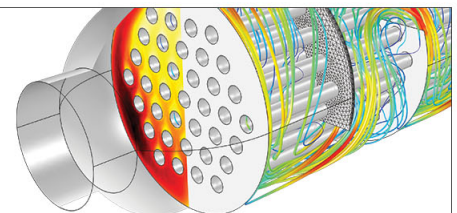
Extending the voltage window in the characterization of electrical transport of large-area molecular junctions

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A large bias window is required to discriminate between different transport models in large-area molecular junctions. Under continuous DC bias, the junctions irreversibly break down at fields over 9 MV/cm. We show that, by using pulse measurements, we can reach electrical fields of 35 MV/cm before degradation. The breakdown voltage is shown to depend logarithmically on both duty cycle and pulse width. A tentative interpretation is presented based on electrolysis in the polymeric top electrode. Expanding the bias window using pulse measurements unambiguously shows that the electrical transport exhibits not an exponential but a power-law dependence on bias. © 2011 American Institute of Physics. [doi:10.1063/1.3608154]

Single molecules or an ensemble of molecules have been incorporated in various molecular junction architectures, which allowed measuring the electrical transport through the molecules.[1] The transport mechanism, however, remains elusive.[2–5] Commonly, non-resonant tunneling has been used to explain the transport.[2,3,6–8] The current density in this case increases exponentially with applied bias. Recently, a power-law dependence has been reported.[4,5] To discriminate between the suggested models, a large bias window is needed. However, characterization at high bias is hampered by irreversible breakdown of the junctions. The origin can be structural changes that the molecules undergo under high voltage, thermal stress, or electrochemical reactions at the electrode.[9–14] These breakdown mechanisms become more pronounced under prolonged application of bias. To eliminate the bias degradation, the measurement time has to be minimized. Here, we use pulse measurements in large-area molecular junctions. We vary the duty cycle and pulse width, compare the pulsed and DC current densities, and determine the breakdown voltage as a function of duty cycle. We show that we are able to extend the bias window, which allows us to discriminate between different electrical transport models in molecular junctions.

We use a previously developed technology of large-area molecular junctions, a reproducible molecular electronic test-bed with yield of almost unity to measure the electrical transport through self-assembled monolayers (SAMs).[15] More than 20 000 molecular junctions were fabricated simultaneously on a single 6-in wafer according to a previously reported semi-automated procedure.[16] On a 6-in Si monitor wafer with a 500 nm SiO$_2$ passivation layer, a 60 nm Au bottom electrode was sputtered onto a Ti adhesion layer and structured by standard photolithography. Vertical interconnects ranging from 1 μm to 50 μm in diameter were defined in insulating photoresist by conventional spin coating and UV lithography. 1-dodecanethiol (C12MT) was dissolved in ethanol using a concentration of 3×10^{-3} M. The self-assembled monolayer was formed inside the vertical interconnects by immersing the wafer in the solution for at least 36 h under N$_2$ atmosphere. Subsequently, a water-based suspension of the conducting polymer poly(3,4-ethylenedioxy-thiophene)-poly(4-styrenesulphonic acid) (PEDOT:PSS), purchased from Agfa-Gevaert, was spincoated. Finally, a 100 nm gold top electrode was thermally evaporated and structured by photolithography. This top contact is utilized as a self-aligned reactive ion etching mask for the removal of the redundant PEDOT:PSS. A schematic presentation of the junction, the layout, and a picture of a finished wafer is shown in Figure 1.

The normalized resistance (RS, in Ω μm^2) at 0.5 V bias was measured in four-point probe geometry in a semi-automatic probe station. DC and pulsed I-V measurements were performed in a probe station (Janis Research Co.) using a Keithley 4200 Semiconductor Parameter Analyzer and a
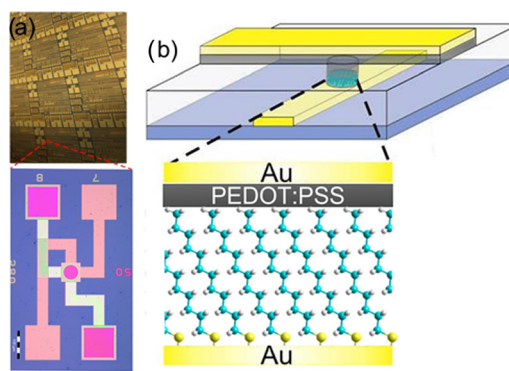

FIG. 1. (Color online) (a) Photograph of a 6-in wafer, showing the repeating units, "dies", and the device layout of a discrete molecular junction (scale bar is 100 μm). (b) A schematic cross section of the molecular junction.
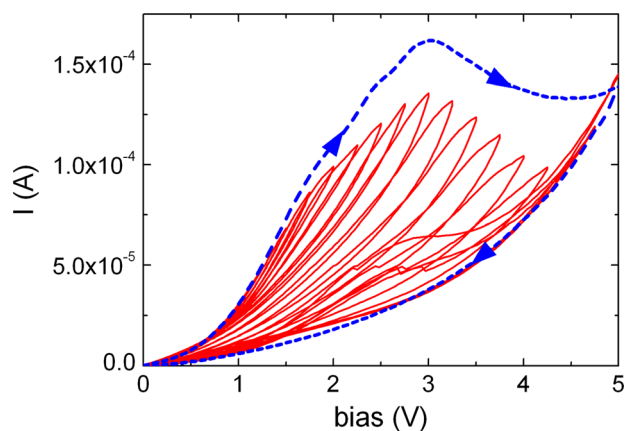
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FIG. 2. (Color online) Current-voltage traces of a C12MT molecular junction measured in air. The device diameter is 10 μm. The dotted line represents the DC measurement directly to 5 V, showing pronounced hysteresis and breakdown of the junction. The inner loops represent consecutive voltage sweeps from 0.25 V to 5 V with a step of 0.25 V on a similar but pristine junction.

Keithley 2602 Source System controlled through Test Script Builder.

The current as a function of DC bias for a typical C12MT large-area molecular junction in air is presented in Figure 2. At low bias, the current is Ohmic. At higher bias, however, a negative differential resistance is observed. The current then decreases with the increasing bias. Furthermore, the measurement shows a huge hysteresis. The diode irreversibly breaks down. Consecutive DC voltage sweeps on a pristine junction show that hysteresis already manifests at low bias, at 1 V to 2 V, and that, after each subsequent measurement, the junction has deteriorated. The degradation is slower when the junction is measured in vacuum but still prohibits application of high DC bias.

To extend the bias window, we performed pulse measurements. The pulse train used is presented in the inset of Figure 3(a). It consists of sequential voltage pulses that increase exponentially to a peak voltage and subsequently decrease similarly. The next pulse train goes to higher peak voltages. This specific pulse train was chosen to check the reversibility and to determine the breakdown voltage. To determine the onset of junction degradation, we varied the duty cycle and the pulse width. Figure 3(a) shows the breakdown voltage as a function of pulse width at a fixed duty cycle of 10%. Each point represents a pristine junction measured in vacuum. The reproducibility is reflected in the lim-

ited scatter in the breakdown voltage, which was taken as the onset of hysteresis in the measurements. The breakdown voltage is logarithmically dependent on pulse width.

Figure 3(b) shows the breakdown voltage as a function of duty cycle for a fixed pulse width of 2 ms for measurements in vacuum and in air. The breakdown voltage increases when the duty cycle decreases; the breakdown voltage is logarithmically dependent on duty cycle. At 100% duty cycle, the breakdown voltage is similar to the value measured under DC bias. The highest breakdown voltage in vacuum corresponds to a breakdown field of about 35 MV/cm. For measurements in air, a similar logarithmic dependence is observed. However, to obtain breakdown voltages as high as those in vacuum, the duty cycle and the pulse width have to be reduced by 2-3 orders of magnitude, which is beyond reach of the experimental setup. The inset of Figure 3(b) shows the difference between pulse and DC bias. The normalized resistance is measured at low DC bias before and after application of 3 V using pulses and DC. The pulse train causes no change in resistance. Subsequent DC measurement at 3 V, however, causes a 100% change in resistance.

Figure 3 shows that the breakdown voltage is logarithmically dependent on both the duty cycle and the pulse width. Alkanethiol SAMs have been reported to undergo dielectric breakdown at fields ranging from 4 MV/cm to 20 MV/cm.[9–12] However, PEDOT:PSS degrades at even lower DC biases. Various mechanisms such as water-assisted dedoping[17] and electrochemical oxidation have been reported. In the last case, the breakdown is due to electrolysis of residual water in the PEDOT:PSS.[13] At a bias above about 2 V, water is oxidized. The gases formed cannot escape because the junction is enclosed in photoresist and sandwiched between a bottom and top electrode (Figure 1(b)). As a result, the pressure rises and the PEDOT:PSS delaminates from the SAM functionalized electrode. The contact area then decreases leading to a decrease in current. We note that, under extreme bias conditions, the junction can literally explode. The degradation depends on the amount of residual water; hence, in air, the onset of breakdown is at lower DC bias and deterioration is faster than in vacuum, as shown in Figure 3.

The junction breaks down due to an integrated Faradaic current that generates a volume of gas leading to delamination. The Faradaic current that is much smaller than the device current depends exponentially on the overpotential,[18] approximately equal to the applied bias. Hence, the breakdown voltage for a given duty cycle depends logarithmically
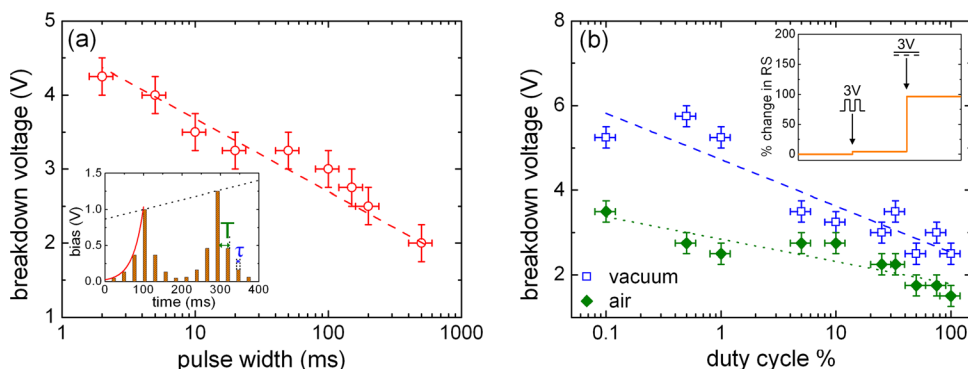

FIG. 3. (Color online) (a) Breakdown voltage as a function of pulse width for 10 μm diameter C12MT molecular junctions measured in vacuum. The duty cycle was fixed at 10%. The inset shows part of the pulse train used. The sequential voltage pulses increase and decrease exponentially around a peak voltage. The peak voltage increases linearly from 0.25 V to 6 V with a step of 0.25 V. (b) Breakdown voltage as a function of duty cycle for similar C12MT junctions in vacuum and in air. The pulse width was fixed at 2 ms. The inset shows the change in the normalized resistance of the junction as a result of pulse and DC measurements at 3 V.
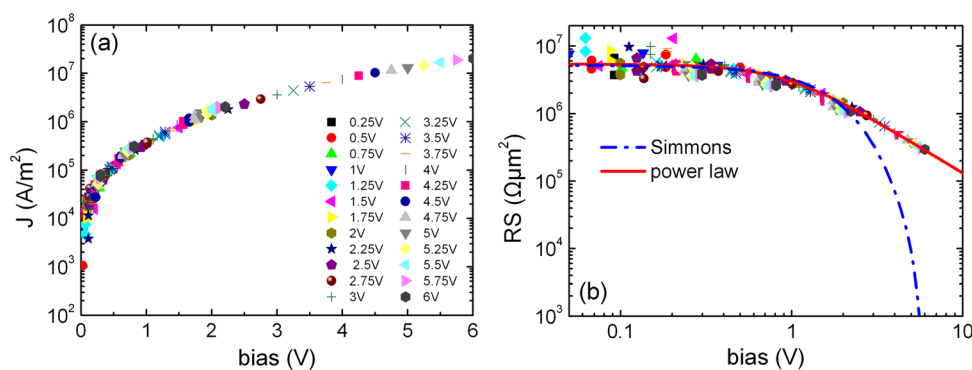
FIG. 4. (Color online) (a) Current density of a typical C12MT molecular junction as a function of bias as determined by pulse measurements. The pulse width was 2 ms and the duty cycle 1%. The peak voltage increased linearly from 0.25 V to 6 V with a step of 0.25 V. (b) Data replotted as normalized resistance as a function of voltage. The drawn curves are fits to the data. The dashed line represents the Simmons model, tunneling through a rectangular barrier with image force included. The solid line represents a power-law dependence of resistance on bias.

on pulse width as shown in Figure 3(a). After each pulse, the gas formed has to diffuse out of the junction. Hence, for a fixed pulse width, a lower repetition rate yields a higher breakdown voltage. The logarithmic dependence of breakdown voltage on duty cycle, Figure 3(b), however, is not yet fully understood. In first order, assuming that the diffusion coefficient is constant, diffusion of the generated volume of gas in the junction shows an exponential dependence on time.[19] The breakdown voltage increases with decreasing duty cycle. At very low duty cycle, the junctions withstand fields as high as 35 MV/cm, indicating that the relevant breakdown mechanism at low voltages is electrolysis of water in the PEDOT:PSS layer and not a field-driven process.

Figure 4(a) shows the current density of a typical C12MT large-area molecular junction up to 6 V bias using pulse measurements. There is no hysteresis. At low bias, below 1 V, pulse and DC measurements overlap, yielding identical values for the normalized resistance. Values derived from all pulse trains going up and down in bias collapse. The junction does not degrade. In Figure 4(b), the data are replotted as normalized resistance as a function of applied bias.

Commonly, non-resonant tunneling has been used to explain the transport. The Simmons model that describes tunneling through a rectangular barrier with image force included[2,7,20,21] is used to fit our data (dashed blue curve in Figure 4(b)). At low bias, a good agreement is obtained. However, at high bias, the Simmons model predicts an exponential decrease in normalized resistance, which is not observed. Recently, a power-law dependence on applied bias has been reported.[4,5,22] The origin could be dissipative tunneling such as environmental Coulomb blockade but is still elusive. The fully drawn red line in Figure 4(b) is a fit of the data with a power-law dependence on bias as discussed for PEDOT-only junctions in Ref. 4. A good agreement is obtained over the whole bias range.

In summary, large-area molecular junctions of dodecanethiol irreversibly break down under continuous applied DC bias of about 1 V to 2 V. By using pulse measurements, however, the bias window could be expanded to more than 6 V. This corresponds to a breakdown field of 35 MV/cm, significantly larger than reported values of 20 MV/cm. The breakdown voltage is shown to depend logarithmically on both the duty cycle and the pulse width. The dependence is tentatively explained by electrolysis in the PEDOT:PSS layer as the breakdown mechanism. Expanding the bias

window using pulse measurements has unambiguously shown that the electrical transport exhibits not an exponential but a power-law dependence on bias.

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