Letter

Stability of large-area molecular junctions

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ABSTRACT

The stability of molecular junctions is crucial for any application of molecular electronics. Degradation of molecular junctions when exposed to ambient conditions is regularly observed. In this report the stability of large-area molecular junctions under ambient conditions for more than two years is presented. Furthermore, the thermal stability of molecular junctions at elevated temperatures is investigated. A transition temperature at 50 °C was observed for molecular junctions based on self-assembled monolayers of alkanedithiols, above which the resistance decreases exponentially with temperature. This transition temperature limits the process window during fabrication and the temperature window during operation.

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The field of molecular electronics has grown exponentially after the seminal theoretical paper of Aviram and Ratner [1], predicting that a single molecule can operate as a rectifying diode. Electronic transport through molecules has since then been investigated experimentally in many different device geometries [2,3]. The most studied systems are self-assembled monolayers (SAMs) of alkane(di)thiols on gold [4–6]. The resistance of Au/SAM Au junctions exponentially increases with increasing molecular length and is independent of temperature, indicating that charge transport is due to non-resonant tunneling [7–9]. Progress in the study of discrete devices is severely hampered by limited reliability, stability, and especially, yield. Electrical shorts in the SAM are readily formed upon vapor deposition of the top electrode [10]. An illustration is the statistical analysis which has been reported for manually measured molecular junctions with a diameter of 2 μm and evaporated metal top electrodes [11]. The yield of the functional junctions was 156 out of 13,440 junctions fabricated, or 1.2%. Formation of shorts can be prevented by applying a conducting barrier layer between the SAM and the top electrode. A yield of unity has been reported for discrete large-area junctions by using the conducting polymer poly(3,4-ethylene-dioxythiophene) stabilized with polystyrene sulphonic acid, henceforth abbreviated as PEDOT:PSS, as a barrier [12]. Even for devices as large as 100 μm in diameter, the PEDOT:PSS layer prevents shorts. The technology is suitable for upscaling, integration and incorporation of functionality. More than 20,000 molecular junctions, discrete and connected in series, were fabricated simultaneously on a single 150 mm wafer in a semi-automated process [13]. Functionality was demonstrated by switchable conductance realized with diarylethene molecular photoswitches

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[14]. A prerequisite for any application is a shelf life extending years. Furthermore, the temperature window for operation needs to be determined. Here we investigate the electrical transport in molecular junctions as a function of storage time and at elevated temperatures.

Discrete large-area molecular junctions were fabricated according to previously published procedure [2,13–16]. By photolithography, vertical interconnects (vias) are created on top of the gold bottom electrodes. A monolayer of alkanedithiols is self-assembled on the exposed gold bottom electrodes within the vertical interconnects. The conducting polymer interlayer of PEDOT:PSS is spincoated on top after the self-assembly process. In the final step Au top electrodes are evaporated and the redundant PEDOT:PSS is etched away with reactive ion etching to prevent parasitic currents. The resulting molecular junctions have the SAM completely encapsulated by photoresist on the sides of the vertical interconnect and protected by the conducting polymer PEDOT:PSS on top. A schematic presentation of the device geometry and a micrograph of an actual junction are presented in Fig. 1.

The current density of C12-dithiol junctions as a function of bias is presented in Fig. 2a. The density is an average over 10 devices, half of them with a diameter of 40 μm and half of them of 80 μm in diameter. The I–V curves of the molecular junctions exhibit a super linear increase due to tunneling, as confirmed by low temperature measurements [7,12]. To investigate the stability of the molecular junctions, the samples were stored in air for subsequent measurements. Molecular junctions have been stored and remeasured after 2.5 years. There is only a minor change of a factor less than two after storage for 888 days, or 2.5 years. In Fig. 2b the resistances of the 10 discrete junctions are presented separately.

To determine the maximum operation temperature, the transport in the junctions was investigated as a function of temperature. The junctions are loaded in the probe station and set under vacuum. The temperature of the system was systematically increased up to 110 °C. The temperature was raised in steps of 10 °C and kept for 5 min at each temperature before performing I–V scans on 2 or 3 junctions at

Fig. 2. Stability of large-area molecular junctions in ambient environment. (a) J–V traces of devices with a C12-dithiol self-assembled monolayer. The average current density is plotted of 10 junctions, where the J–V characteristics from the junctions after processing (■) are compared to the same junctions stored in air for 888 days (◇). The normalized resistance at 0.1 V for the 10 measured individual junctions of 40 and 80 μm in diameter is presented in (b). No dependence on device area is observed for the small increase in resistance after almost 2.5 years storage in air.
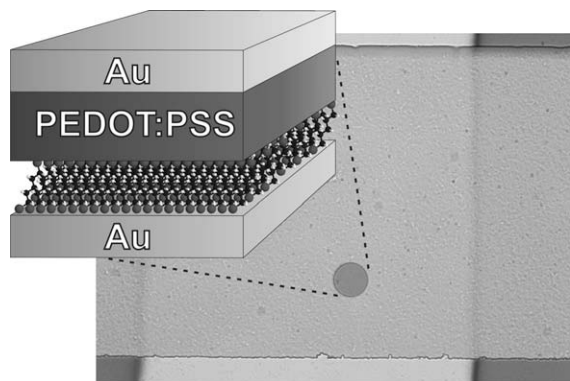

Fig. 1. A micrograph of a molecular junction of 100 μm in diameter. In this image the top Au electrode is 20 nm thick and therefore partially transparent. A schematic representation of the junction with the stacked layers of Au/SAM/PEDOT:PSS/Au is shown in the inset.
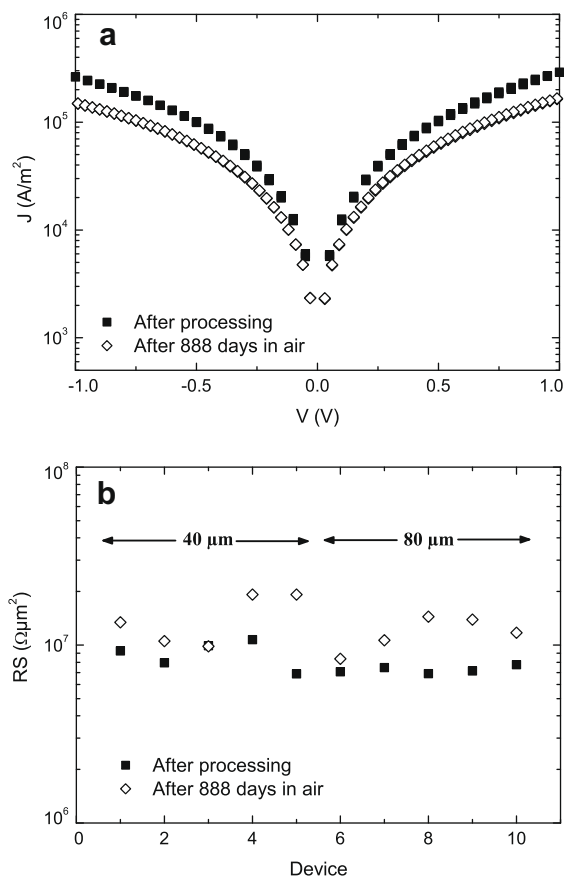
these temperatures. Subsequently, the temperature was raised and kept constant for 5 min again, before performing the next measurements.

Fig. 3a shows the normalized resistance as a function of anneal temperature. Data are presented for different lengths of the alkanedithiols, i.e. C8, C10, C12, and C14. For comparison a junction without a SAM present (PEDOT:PSS-only device) is included. The resistances of all junctions decrease with increasing anneal temperature. We note that the change in resistance is irreversible. Since the maximum temperature inside the probe station is 110 °C, the samples were annealed at 150 °C and 200 °C for 15 min on a hotplate in air to investigate the decrease in resistance at higher temperatures. Towards high temperatures, all junctions approach the resistance value of a PEDOT:PSS-only device. The transition temperature is defined as shown in Fig. 3b, by the intercept between low and high temperature fits. Surprisingly, the transition temperature does not depend on the length of the molecules and is at 50 °C for all junctions. Below this temperature
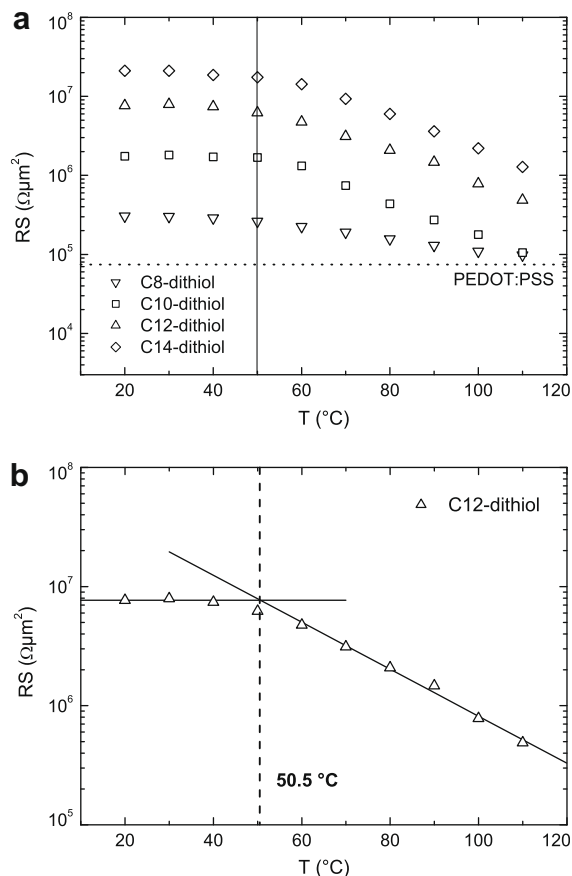
Fig. 3. (a) Normalized resistance at 0.1 V, *RS*, as a function of increasing temperature. For alkane(di)thiols with lengths C10, C12, and C14 a similar trend is observed with increasing temperature, independent of molecule length. C8 shows a different trend since the normalized resistance approaches that of PEDOT:PSS only junctions (represented by the dotted line) at higher temperatures. All SAMs show a transition temperature around 50 °C, after which the resistance is decreasing exponentially with increasing temperature. (b) The transition temperature is determined by calculating the intersection between the average *RS* value of 20–40 °C and the linear fit to the data for 70–110 °C.

no changes in resistance are observed. Above the transition temperature the resistance decreases exponentially with increasing temperature.

The formation of shorts due to PEDOT:PSS filaments can be excluded. When conducting filaments of PEDOT:PSS would form at a specific temperature, irrespective of the length of the SAM, the decrease in resistance would be more pronounced for higher resistances, hence longer molecules.

Thermal stability of SAMs on Au surfaces has been studied extensively [17–23]. Phase transitions and desorption of alkanethiol monolayers on Au(1 1 1) have been observed at elevated temperatures with STM [20,21,24–27]. The two dimensional melting temperature of alkanethiol SAMs increases with increasing chain length of the alkane backbone [22,23,27]. The transition temperature in the junctions being independent of chain length can therefore not yet be explained. The formation of an incommensurate

phase as observed by Fenter and coworkers is similar to our observations [28]. While absolute transition temperatures are strongly dependent on coverage of the monolayer, the temperature for the commensurate–incommensurate phase transition is shown to be independent of molecular length, however, only for *n*-alkanethiols with $n \geqslant 14$.

To summarize, we investigated the stability of large-area molecular junctions at temperatures up to 110 °C. Long term stability at room temperature was demonstrated, when stored in ambient conditions. After 888 days in air without UV shielding or any other precautions, no significant change was observed in the current–voltage characteristics of molecular junctions. At elevated temperatures, a transition point was found at 50 °C, which is independent of the molecule length. Up to 50 °C no changes in resistance are observed, whilst above the transition temperature a decrease of the normalized resistance was observed. The observed exponential decrease in resistance for temperatures exceeding 50 °C is similar for all SAMs irrespective of the molecular length of the alkanedithiols. The upper limit of 50 °C is a strong limitation for the applicability of molecular electronics.

Acknowledgements

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