High-bias breakdown of Au/1,4-benzenedithiol/Au junctions

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We have studied the high-bias breakdown of Au/1,4-benzenedithiol (BDT)/Au junctions at room temperature. Exploiting the break junction technique, we held a Au/BDT/Au junction and ruptured it by applying a voltage ramp. The conductance first changes gradually with the bias and then abruptly increases at breakdown. We found that the breakdown voltage shows a broad distribution and takes a maximum at ~(1.2–1.5)V. The breakdown voltage is unaffected by the ambient atmosphere but tends to slightly decrease with increasing the junction conductance. We consider that the Au electrode becomes unstable at the breakdown voltage and collapses to crush the junction. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2976666]

High-bias breakdown of molecular junctions is not only a subject of practical importance but also a physical phenomenon of academic interest because it involves many unique processes such as the heating of electrons and ions,[1,2] the excitation of molecular vibrations,[3] and the weakening of the molecule-electrode coupling.[4] For 1,4-benzenedithiol (BDT) junctions, Di Ventra *et al.*[3] theoretically studied molecular vibrational modes under high bias and showed that the BDT-electrode coupling becomes significantly weakened around 5 V, leading to a decrease in the junction current at higher biases. In experiment, Reed *et al.*[5] measured the *I-V* characteristics of Au/BDT/Au junctions up to 6 V and observed the buildup of current fluctuations above 3 V. However, subsequent *I-V* experiments have explored low-bias characteristics of Au/BDT/Au and rarely covered the high-bias regime above 1 V, except a suggestion of junction instability around ±1.2 V.[6] To fill up this knowledge gap, we have made in this work the direct measurement of the break voltage of Au/BDT/Au junctions at room temperature. Since the bias and the tensile force are two major factors affecting the junction breakdown,[7] our high-bias break experiment complements the recent tensile break experiments on Au/alkanedithiol/Au[8–10] and Au/BDT/Au[11] junctions.

The experimental procedures are basically the same as we used before for measuring the conductance of Au/BDT/Au junctions.[12] We exploited the mechanically controllable break junction technique and broke a Au wire of 0.3 mm in diameter to form a pair of nanogapped electrodes. After exposing the electrodes to the ethanol solution containing ~1 mM BDT molecules for a couple of minutes, the junction was immediately loaded into a vacuum chamber which was first evacuated to $\sim 10^{-3}$ Pa and then backfilled with Ar gas. We held the junction at a specified conductance state under a constant bias V_0. Then we increased the bias from 0 to 5 V and monitored the corresponding change in the conductance. We discarded all conductance data on unstable junctions and retained only those that satisfy the criterion that the conductance resumes its initial value when the bias ramp reaches V_0.

We observed a variety of breakdown behaviors. In most cases, the conductance jumps up at a certain threshold bias, which we define as the breakdown voltage V_{bd}. After this abrupt increase, the conductance sometimes decreases to zero either immediately or after showing irregular ups and downs. In other cases, the conductance jumps up and does not drop back, as shown in Fig. 1, unless we increase the electrode separation, i.e., the junction becomes short circuited. Former breakdown mostly appears for $V_0 \geq 0.8$ V, while the short-circuit breakdown is abundant at 0.1 V. Figure 2 summarizes the break voltage data obtained at $V_0 = 0.1$ V in Ar atmosphere. Three histograms are obtained on conductance states of $0.004G_0$, $0.01G_0$, and $0.1G_0$ ($G_0 \equiv 2e^2/h$ is the quantum unit of conductance) and constructed from 150, 125, and 44 break measurements, respectively. In all histograms, V_{bd} shows a broad distribution spanning from 0.5 to 2.5 V and shows a maximum around 1.2–1.5 V. We plot in Fig. 3 the average breakdown voltage $\langle V_{bd} \rangle$ as a function of the junction conductance. Although each data point has a large statistical uncertainty, the plot clearly indicates that $\langle V_{bd} \rangle$ tends to decrease with increasing the junction conductance. We also measured the break voltage at $V_0 \geq 0.8$ V in air and helium atmosphere. Because of the increased junction instability at higher biases, we could not obtain many V_{bd} data in these measurements. Nevertheless, our results suggested that $\langle V_{bd} \rangle$ is insensitive to the ambient atmosphere and tends to increase with V_0. The latter behavior of $\langle V_{bd} \rangle$ is not unexpected since applying high V_0 automati-

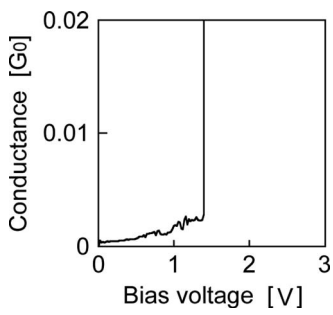

FIG. 1. Typical conductance change in the high-bias breakdown.

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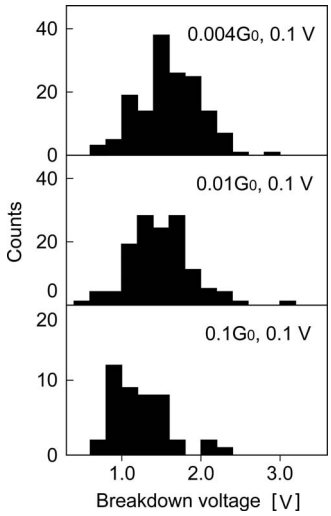

FIG. 2. Distribution of the breakdown voltage measured on different conductance states at V_0=0.1 V.

cally eliminates junctions of lower V_{bd} and results in pushing up $\langle V_{bd}\rangle$.

It is generally believed that the conductance of the Au/BDT/Au junction sensitively increases with the Au–S coupling strength at the BDT/Au interface. Thus, if the junction fails at the interface, junction states of higher conductance would show higher break voltage. In Fig. 3, however, the observed $\langle V_{bd}\rangle$ varies ~25% when the junction conductance changes by a factor of 25. Also, $\langle V_{bd}\rangle$ tends to *decrease* with increasing the junction conductance. The high-bias breakdown at the BDT/Au interface thus seems unlikely. Alternatively, we consider that the observed conductance jump at V_{bd} is caused by instability within the Au electrodes. Huang *et al.*[8–10] showed that the tensile fracture of Au/octanedithiol/Au junctions takes place not at the Au–S bond but at the nearby Au–Au bond in the electrode, which is weaker than the Au–S bond.[13] Also, Lörtscher *et al.*[6] reported the high ductility of the Au electrodes under high biases. Considering these observations, the partial collapse of the Au electrode would be a plausible assumption. The electrode collapse is also consistent with the abundance of the short-circuit breakdown shown in Fig. 1.

The driving mechanism of the electrode breakdown, however, remains unclear. The result shown in Fig. 3 indicates that the break voltage has a negative correlation with the junction conductance, or the junction current. This naturally suggests current-induced effects such as electromigration and local heating. The electromigration of Au electrode

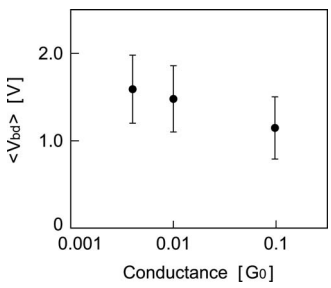

FIG. 3. Average breakdown voltage at 0.1 V plotted as a function of the junction conductance. Each error bar represents the standard deviation of the corresponding distribution of V_{bd} shown in Fig. 2.

atoms, however, appears unlikely because of low junction currents. In Fig. 1, for example, the junction current at V_{bd} is ~0.3 μA which is orders of magnitude lower than the current level (~100 μA) sustainable by pure-Au atomic junctions.[14] Concerning the local junction heating, previous experiments on Au/alkanedithiol/Au show $\Delta T \sim 30$ K at 1 V.[8–10] For Au/BDT/Au junctions, exponential dependence of the electron-phonon coupling parameter γ on molecular length[8–10] suggests $\gamma \sim 600$ K $V^{-1/2}$ for short BDT, yielding the estimation $\Delta T \sim 309$ K at 1 V. On the other hand, efficient heat transfer from the junction to the electrode bulk predicts $\Delta T = 16$ K at 1 V when the Au electrode is at 0 K.[1] We, therefore, have no solid ΔT data on Au/BDT/Au and have to wait further experimental studies (e.g., junction stretching experiment[8–11] under high biases) to know whether ΔT at V_{bd} is sufficiently high for inducing the thermal breakdown.

According to the thermal activation model of junction breakdown,[7,14] the activation barrier is reduced by both the bias and the tensile force. Tsutsui *et al.*[11] recently demonstrated that the stability of Au/BDT/Au junctions depends on the tensile force. Thus, the tensile force can assist the high-bias break of Au/BDT/Au and affect V_{bd}. Smit *et al.*[14] attributed the distribution of V_{bd} of Au single-atom chains to the variation of the tensile force. Because the V_{bd} distributions shown in Fig. 2 are similar to that of Au atomic chains, the tensile force is also likely to affect V_{bd} of Au/BDT/Au and broadens its distribution. The tensile force in the electrode would drive Au atoms toward the molecule and can account for the abundance of the short-circuit breakdown. If the high-bias breakdown is tensile force assisted, the result shown in Fig. 3 suggests that the tensile force should increase with the conductance. Since the higher-conductance state of Au/BDT/Au has stronger Au/BDT coupling and shorter electrode-electrode distance,[15] the suggested positive correlation between the force and the conductance appears plausible and awaits further experimental verification.

In summary, we have studied the high-bias breakdown of the Au/BDT/Au junctions at room temperature and found that the junction becomes unstable at V_{bd} ~(1.2–1.5)V. The observed V_{bd} shows a broad distribution which shifts to the low-bias side with increasing the junction conductance. We consider that the Au electrode(s) partially collapses at V_{bd} and shunts the junction. The breakdown mechanism still remains unclear, and further experiments on ΔT and the tensile force would be required to single out the most contributing factor(s) for the high-bias breakdown. Our results indicate that not BDT but the Au electrode determines the maximum junction rating. Thus, for increasing the bias limit and studying the intrinsic breakdown characteristics of BDT, we have to look for non-Au electrodes[16] that can achieve both high electron transmission against BDT and superior stability against high biases.

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