<table>
<thead>
<tr>
<th>Title</th>
<th>High-bias breakdown of Au/1,4-benzenedithiol/Au junctions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Teramae, Yumi; Horiguchi, Kazunori; Hashimoto, Shuhei; Tsutsui, Makusu; Kurokawa, Shu; Sakai, Akira</td>
</tr>
<tr>
<td>Citation</td>
<td>APPLIED PHYSICS LETTERS (2008), 93(8)</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2008-08-25</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/84603">http://hdl.handle.net/2433/84603</a></td>
</tr>
<tr>
<td>Rights</td>
<td>Copyright 2008 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.</td>
</tr>
<tr>
<td>Type</td>
<td>Journal Article</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
</tbody>
</table>
High-bias breakdown of Au/1,4-benzenedithiol/Au junctions

Yumi Teramae, Kazunori Horiguchi, Shuhei Hashimoto, Makusu Tsutsui, Shu Kurokawa, and Akira Sakai

Department of Materials Science and Engineering, Graduate School of Engineering, Kyoto University, Sakyoku, Kyoto 606-8501, Japan

(Received 22 April 2008; accepted 2 August 2008; published online 29 August 2008)

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.5 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.6 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/Au8–10 and Au/BDT/Au11 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 ~10−3 Pa and then backfilled with Ar gas. We held the junction at a specified conductance state under a constant bias V0. 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 V0.

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 Vbd. 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 V0 ≥ 0.8 V, while the short-circuit breakdown is abundant at 0.1 V. Figure 2 summarizes the break voltage data obtained at V0 = 0.1 V in Ar atmosphere. Three histograms are obtained on conductance states of 0.004G0, 0.01G0, and 0.1G0 (G0 = 2e2/h is the quantum unit of conductance) and constructed from 150, 125, and 44 break measurements, respectively. In all histograms, Vbd 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 ⟨Vbd⟩ as a function of the junction conductance. Although each data point has a large statistical uncertainty, the plot clearly indicates that ⟨Vbd⟩ tends to decrease with increasing the junction conductance. We also measured the break voltage at V0 ≥ 0.8 V in air and helium atmosphere. Because of the increased junction instability at higher biases, we could not obtain many Vbd data in these measurements. Nevertheless, our results suggested that ⟨Vbd⟩ is insensitive to the ambient atmosphere and tends to increase with V0. The latter behavior of ⟨Vbd⟩ is not unexpected since applying high V0 autami-

FIG. 1. Typical conductance change in the high-bias breakdown.
atoms, however, appears unlikely because of low junction currents. In Fig. 1, for example, the junction current at \( V_{bd} \) is \(-0.3 \mu A\) which is orders of magnitude lower than the current level (\(-100 \mu A\)) sustainable by pure-Au atomic junctions.\(^{14}\) Concerning the local junction heating, previous experiments on Au/alkanedithiol/Au show \( \Delta T \approx 30 \) K at 1 \( V \). For Au/BDT/Au junctions, exponential dependence of the electron-phonon coupling parameter \( \gamma \) on molecular length\(^{8-10}\) suggests \( \gamma \approx 600 \) K V\(^{-1/2}\) for short BDT, yielding the estimation \( \Delta T \approx 309 \) K at 1 V. On the other hand, efficient heat transfer from the junction to the electrode bulk predicts \( \Delta T \approx 16 \) K at 1 V when the Au electrode is at 0 K.\(^{1} \)

We, therefore, have no solid 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 \( \Delta T \) at \( V_{bd} \) is sufficiently high for inducing the thermal breakdown.

According to the thermal activation model of junction breakdown,\(^{7,10}\) 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 high-conductance state of Au/BDT/Au has stronger Au/BDT coupling and shorter electrodes-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 \( V_{bd} \approx (1.2-1.5) V \). 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 \( \Delta T \) 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.

This work was supported by KAKENHI (No. 18041008).

---


\(^{5}\)M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, Science...
278, 252 (1997).