Vibrational spectra of metal-molecule-metal junctions in electromigrated nanogap electrodes by inelastic electron tunneling

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We measure the vibrational signatures of metal-molecule-metal junctions formed from 1,8-octanedithiol and 1,4-benzenedithiol incorporated into electromigrated nanogap electrodes using inelastic electron tunneling spectroscopy (IETS). The junction conductance measured suggests that the IETS spectra have been achieved at the individual molecule level. The IETS spectra provide unambiguous experimental evidence of the existence of the component molecules in the fabricated nanogap electrode testbeds. The intense Au–S stretch peaks elucidate that the thiol anchor group is linked to the broken Au wires during electromigration, thus creating reliable electrical contact to individual molecules. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3097217]

Over the past decades, tremendous progress has been made in charge transport characterization of individual molecules bridged between metallic electrodes.[1] Inelastic electron tunneling spectroscopy[2] (IETS) has recently become a powerful tool for investigating metal-molecule-metal junctions,[3–14] which are being examined as potential building blocks for molecular electronic systems. The IETS provides not only *in situ* characterization technique to identify the molecules associated with charge transport in such junctions but also important insight into how the interaction of tunneling charge carriers with molecular vibrational modes influences the overall charge transport characteristics. Most of the IETS studies have been performed on the basis of ensemble average of an enormous number of molecules in the junctions.[5–8,10,12,13] Although it has also become possible to measure vibrational structures even on a single molecule employing scanning tunneling microscopy (STM),[4] mechanical[11] or STM break junction,[14] and in three-terminal device,[9] the IETS measurement at the individual level of the molecules of interest seems to be still challenging due to the difficulty of making reliable electrical contact to individual molecules.

In the present study, we report on the vibrational spectra of metal-molecule-metal junctions formed from 1,8-octanedithiol (ODT) and 1,4-benzenedithiol (BDT) incorporated into electromigrated nanogap electrodes,[15] utilizing the IETS technique in order to explore the molecular vibrations in these junctions. Even if the electromigration is a widely adopted technique to achieve reliable electrical contact to individual molecules (single or at least a few molecules),[9,15,16] a full line spectrum and detailed vibration assignments of IETS in the electromigrated molecular junctions have not been reported.[17] Furthermore, the presence of the molecules of interest at the nanogap electrode is problematic due to the stochastic nature of the electromigration process.[18] Our IETS data are capable of unambiguously identifying the presence of molecules bridged in the elec-

tromigrated nanogap electrodes, as will be evidenced by completely assigned vibrational spectra of the constituent molecules in the metal-molecule-metal junctions.

The devices are fabricated using electromigration-induced break-junction technique.[15] Electron-beam lithography and lift-off are used to create continuous thin metal (1 nm Cr/15 nm Au) wires with widths of about 50 nm at their narrowest constriction [Fig. 1(a)]. After cleaned in oxygen plasma for 1 min, the samples are immersed in a dilute solution (1 mM) of ODT and BDT in 10 mL ethanol for 24 h. The molecular deposition is done on the gold surface in the solution inside a nitrogen-filled glovebox with an oxygen level less than 10 ppm. Before use, each sample is rinsed in ethanol and gently blown dry in a nitrogen stream to remove noncovalently attached molecules. We cool the samples coated with the molecules to 4.2 K in a vacuum cryostat and then the electromigration proceeds to form electrode pairs with a nanometer-scale separation by ramping up a dc voltage across the wire while monitoring the resistance. The voltage is ramped until a substantial increase in the resis-
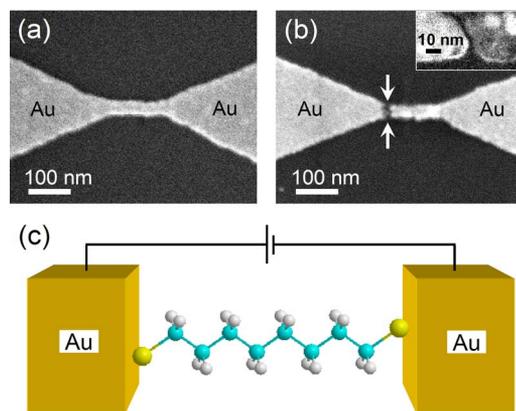
FIG. 1. (Color online) Scanning electron microscopy (SEM) image of (a) a continuous Au wire before electromigration and (b) a broken Au wire after electromigration. The inset shows the high resolution SEM image focusing on a broken nanogap. (c) Schematic of a final device incorporating an ODT molecule.

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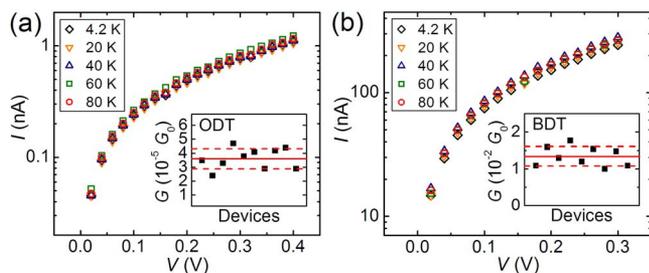
FIG. 2. (Color online) Semilog plots of temperature-variable *I-V* characteristics of (a) Au-ODT-Au and (b) Au-BDT-Au junctions at selected temperatures (4.2, 20, 40, 60, and 80 K). The insets show the statistical distribution of measured conductance (see text for details).

tance is observed upon which the applied voltage is rapidly set to zero.[16] This feedback loop is repeated to reach the target resistance of the nanometer-gap tunnel junctions (normally more than several MΩ). This produces a gap with about 1–2 nm [see the inset of Fig. 1(b)], across which molecules are often connected. Schematic of a final device is illustrated in Fig. 1(c).

Figure 2 shows the temperature-variable current-voltage (*I-V*) data for Au-ODT-Au and Au-BDT-Au junctions formed in the electromigrated nanogap electrodes, obtained between 4.2 and 80 K. No temperature dependence of the currents was observed, which confirms that tunneling is the transport mechanism for these junctions in the bias range measured. So far, a coherent picture has emerged for the nonresonant tunneling mechanism at the low-bias regime through alkyl chains[19,20] and a family of phenyl molecules.[21,22] The observed tunneling transport can be reasonably expected because the Fermi energy of the electrode lies deep within the highest occupied molecular orbital-lowest unoccupied molecular orbital gap of short molecules, which gives rise to a considerable energy barrier against charge transport.

The insets of Fig. 2 display the conductance values (*G*) measured for the ODT (ten devices) and BDT (nine devices) junctions. The solid lines represent the mean conductance and the dashed lines show the standard deviation across the

individual measurements. The conductance was obtained by means of the least-squares linear fit within the low-bias linear region (0–0.1 V) of the *I-V* characteristics. The mean conductance with the standard deviation is estimated to be $(3.62 \pm 0.75) \times 10^{-5} G_0 (=2e^2/h)$ for ODT and $(1.34 \pm 0.27) \times 10^{-2} G_0$ for BDT. Collectively, from comparing the estimated values and the error range of the electrical conductance with previous reports,[23–26] we can infer that there are single or at least a few molecules in the electromigrated nanogap junctions.

Figure 3 shows the *I-V* curve, the differential conductance (*dI/dV*), and the IETS (d^2I/dV^2) spectrum of Au-ODT-Au and Au-BDT-Au junctions measured at 4.2 K. Although the *I-V* characteristics seem to be linear over the bias range measured, the plots of *dI/dV* and d^2I/dV^2 exhibit significant features corresponding to vibrational modes of the molecules under investigation. Standard ac modulation techniques with a lock-in amplifier are utilized to directly obtain the first and second harmonic signals proportional to *dI/dV* and d^2I/dV^2, respectively.[2,27] In IETS, the vibrational modes of the molecules present in the junction are detected by their influence on the current through the tunnel barrier. A molecular vibration coupled to tunneling charge carriers gives rise to an increase in slope of the *I-V* curve owing to inelastic electron tunneling process, which then appears as a step and peak in the first (*dI/dV*) and second (d^2I/dV^2) derivatives.

The IETS spectrum of Au-ODT-Au junction shown in Fig. 3(c) is stable and reproducible upon successive bias sweeps. In order to aid the assignments of the vibrational modes in IETS spectra, we performed density functional theory calculations on the free thiolate form of the molecules under investigation.[27] Also, the vibrational modes can be extensively assigned by comparison with previously reported infrared, Raman, and IETS measurements.[27] The most pronounced vibrational mode is the $\nu(C-H)$ stretch at 355 mV. The strong peak of the $\nu(C-H)$ mode in the ODT junction suggests that the intensity of the $\nu(C-H)$ peak does not arise solely from the presence of the terminal methyl (CH$_3$) group of the alkanemonothiols.[12,13] A simulated IETS calculation based on nonequilibrium Green's function formalism has
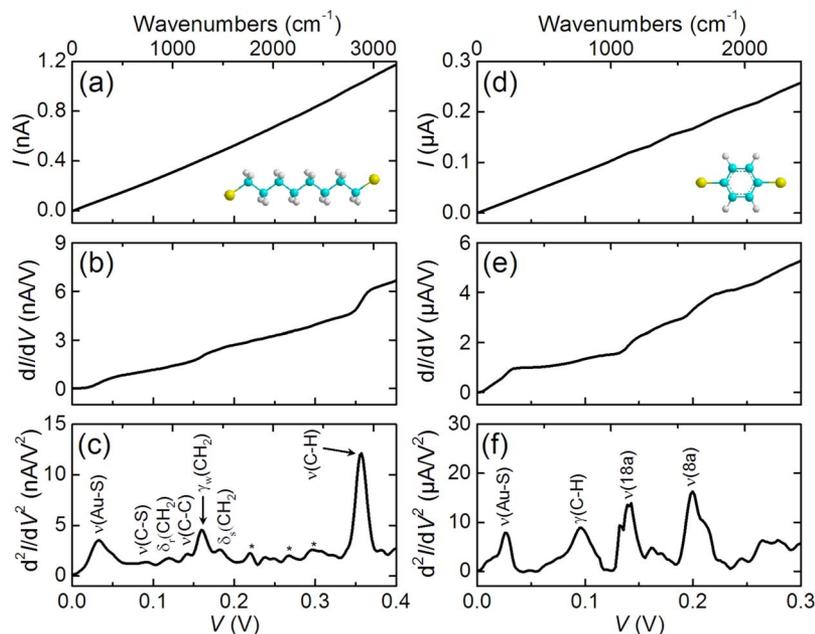
FIG. 3. (Color online) Transport properties of Au-ODT-Au [(a)–(c)] and Au-BDT-Au [(d)–(f)] junctions measured at 4.2 K. [(a) and (d)] *I-V* characteristics. The insets display the chemical structure of each molecule. [(b) and (e)] Differential conductance (*dI/dV*) obtained from lock-in first harmonic signal. [(c) and (f)] IETS spectrum (d^2I/dV^2) obtained from lock-in second harmonic signal. The peaks are labeled with their assigned vibrational modes. The asterisks are modes likely associated with the free thiol group. Benzene ring modes are given in terms of Wilson–Varsanyi terminology (Ref. 33).

also suggested that depending on the geometry binding thiol anchor on Au surface, the peak intensity of the ν(C–H) mode may be strong or weak.[28] The full width at half maximum of the ν(C–H) peak is identified to be 16 mV by fitting a Gaussian distribution function, which is reasonably consistent with the theoretically expected peak width for the measurement condition (at 4.2 K with ac modulation amplitude of 7.8 mV).[29] We also observe a variety of lower energy vibration modes in the region from 30 to 200 mV. The prominent peak at 31 mV is assigned to ν(Au–S) stretching mode,[30] which elucidates that the thiol anchoring group of ODT molecules is reacted with the Au nanogap electrodes, creating robust metal-molecule contacts. Peaks are also reproducibly observed at 92, 119, 143, 161, and 181 mV. These correspond to ν(C–S) stretching, δr(CH$_2$) rocking, ν(C–C) stretching, γ_w(CH$_2$) wagging, and δ_s(CH$_2$) scissoring modes, which are associated with vibrations for an aliphatic alkyl moiety of ODT.

The IETS spectrum of Au-BDT-Au junctions is shown in Fig. 3(f). For the BDT junction, we observe three prominent peaks in the IETS spectrum at 97, 141, and 199 mV. These vibrations are assigned to γ(C–H) aryl out-of-plane bending, ν(18a) stretching, and ν(8a) stretching modes, which originated from the vibrational modes of the benzene ring.[8,10,31] A theoretical study predicted that the ν(18a) and ν(8a) ring modes should have the strong vibronic coupling in biphenyl molecules,[32] and this was experimentally observed for other conjugated molecular wires[8,10] that coincide with our result. The Au–S stretch peak at 27 mV also implies that the molecule is reliably trapped between the broken electrode pairs during electromigration by the Au-thiol anchoring bond architecture.[30]

All the peak assignments for molecular vibrations observed in this study are listed in Table SI.[27] The fully assigned IETS spectra corresponding to molecular vibrational modes not only identify the existence of the component molecules in the electromigrated nanogap electrodes but also manifest that the molecules play a direct role in charge transport through metal-molecule-metal junctions.

In summary, we demonstrated the measurements of the completely assigned vibrational spectra for Au-ODT-Au and Au-BDT-Au junctions formed in the electromigrated nanogap electrode testbeds by using IETS technique. The estimated conductance implies that the measurements have been done at the individual molecule level. We observed that the IETS spectra are clearly sensitive to the chemical structures of the molecules: the spectrum of the ODT junction is dominated by an aliphatic alkyl moiety, whereas aromatic ring modes are prominent in the BDT junction. In both two types of metal-molecule-metal junctions, the Au–S stretch mode is apparent, suggesting that a reliable metal-molecule contact is formed.

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