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Inelastic electron tunneling spectroscopy for molecular detection

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Inelastic electron tunneling spectroscopy (IETS) [R. C. Jaklevic and J. Lambe, Phys. Rev. Lett. **17**, 1139 (1966); R. G. Keil *et al.*, Appl. Spectrosc. **30**, 1 (1976); K. W. Hipps and U. Mazur, J. Phys. Chem. **97**, 7803 (1993); U. Mazur *et al.*, Anal. Chem. **64**, 1845 (1992); P. K. Hansma, *Tunneling Spectroscopy* (Plenum, New York, 1982)] measurements are performed on Si nanowire (NW)/SiO₂/Al NW tunnel junctions. The tunnel junction area is $\sim 50 \times 120$ nm and tunneling occurs across a 10 nm thick SiO₂ layer. IETS measurements are performed at 300 K for ammonium hydroxide (NH₄OH), acetic acid (CH₃COOH), and propionic acid (C₃H₆O₂) molecules. The *I–V*, *dI/dV–V*, and *d²I/dV²–V* characteristics of the tunnel junction are measured before and after the adsorption of molecules on the junction using vapor treatment or immersion. Peaks can be observed in the *d²I/dV²–V* characteristics in all the cases following molecules adsorption. These peaks may be attributed to vibrational modes of N–H and C–H bonds. © 2014 American Vacuum Society. [http://dx.doi.org/10.1116/1.4897137]

I. INTRODUCTION

Inelastic electron tunneling spectroscopy (IETS) provides a means to characterize the phonon spectrum of molecules by measuring phonon-assisted tunneling current through a potential barrier impregnated with the molecules of interest.^{1–5} Traditionally, this technique has used metal/ insulator/metal (MIM) junctions and molecules are adsorbed on to the insulator during junction fabrication. At low applied voltage V, tunneling through the barrier is elastic. However, inelastic tunneling caused by electron interaction with vibrational states in the adsorbed molecules creates additional conduction channels, with a change in energy $\hbar\omega$. These lead to peaks in the d^2I/dV^2 vs V characteristics for each additional channel, providing a spectrum of the molecular vibrational modes (Fig. 1). As energy separations in the vibrational spectrum are relatively small compared to the electronic spectrum, in many cases the full vibrational spectrum can be measured only at low tempera $ture^4 < 30$ K. However, it may be possible to measure part of the spectrum even at room temperature, raising the possibility of a molecular detector.

IETS may provide a spectroscopic technique with high sensitivity and selectivity⁶ for gas sensing.⁷ However, the use of IETS for sensing applications requires molecule adsorption only after device fabrication. Bommisetty *et al.* have measured and contrasted the full IETS characteristics for an NH₃ doped, $20 \times 20 \,\mu$ m Al/Al₂O₃/Pb junction at 4 K, with the corresponding characteristic at 300 K.^{7,8} Two large peaks corresponding to Al-O and NH₃ phonons persist even at 300 K, providing a means to identify the underlying molecules bonds.⁸ More recently, the IETS molecular spectra have been measured using scanning tunneling microscopy (STM–IETS).^{9–11} This allows the characterization of single molecules with simultaneous imaging of the surface with atomic resolution,⁹ e.g., STM

measurements have been performed on single acetylene molecules.⁹ Single molecule spectra have also been measured using micrometer scale metal/molecule/metal junction measurements of alkyl and π -conjugated molecules,¹² and nanoscale alkanedithiol monolayers.¹³

In this paper, IETS measurements are presented for nanoscale semiconductor/insulator/metal tunnel junctions [Si nanowire (NW)/SiO₂/Al NW] (Fig. 2). Our use of a Si NW provides a means to define a more robust tunnel junction with the potential for gate control. The molecules of interest are adsorbed on to the insulator after device fabrication. At low applied voltage, the tunneling process is similar to a MIM device. However, as the applied voltage increases, the electrical characteristics are affected by the Schottky barrier formed at the Si NW surface. With a reverse biased Schottky barrier, IETS peaks may be measured at reduced current, with less likely hood of damaging the tunnel junctions.

IETS measurements are performed on wellcharacterized molecules such as NH₄OH, CH₃COOH, and C₃H₆O₂ at room temperature. The *I*–*V*, *dI*/*dV*–*V*, and *d*²*I*/ *dV*²–*V* characteristics of the tunnel junction are measured before and after the adsorption of the ammonium hydroxide (NH₄OH), acetic acid (CH₃COOH), and propionic acid (C₃H₆O₂) molecules using vapor treatment for NH₄OH molecules and immersion for CH₃COOH and C₃H₆O₂ molecules.

II. FABRICATION

Nanoscale (Si NW/SiO₂/Al NW) tunnel junctions were fabricated using electron beam lithography (EBL). Here, the Si NW (Refs. 14–16) was fabricated in heavily doped n-type silicon-on-insulator (SOI) material (doping density $\sim 10^{19}-10^{20}$ /cm³). Spin-on-doping was used to dope the top Si of the SOI material. Following this, a nanowire pattern was written using EBL in PMMA resist with a molecular weight of 950 000, diluted 2% in Anisole. A 40 nm thick Al

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FIG. 1. (Color online) Schematic diagrams of (a) inelastic tunneling and (b) IETS signals (The *I*–*V* characteristics, conductance G = dI/dV - V and IETS peaks $d^2I/dV^2 - V$) for a metal/insulator/metal tunnel junction device.

layer was then evaporated and lift-off used to create a \sim 50 nm wide Al NW. This created a hard mask for reactive ion etching (RIE) of the top Si layer. SF₆ was used as the RIE gas at 100mTorr for 40 s, at RF power of 100 W and an etch depth of 200 nm was obtained. The Al mask was then removed using wet etching for 30 s. Here, the wet-etch contained mixtures of 1%-5% HNO₃ for Al oxidation, 65%-75% H₃PO₄ to dissolve the Al₂O₃, 5%-10% CH₃COOH for wetting and buffering and H₂O dilution. Si NWs with lengths $\sim 1 \,\mu m$ and widths down to $\sim 50 \,nm$ were fabricated by this process. The NWs were then thermally oxidized at 1000 °C to create a SiO₂ surface layer \sim 10 nm thick. A second EBL stage was then used to define a 40 nm thick and $\sim 120 \text{ nm}$ wide Al NW such that it crossed the Si NW, forming the nanoscale Si NW/SiO₂/Al NW tunnel junction. Figure 3 shows scanning electron micrograph (SEM) of a complete device.

The reduction in device dimension to the nanoscale is expected to increase the sensitivity of the device to molecules adsorbed on the tunnel junction. Various mechanisms are possible for adsorption of molecules on the tunnel junction: The top Al layer is only ~40 nm thick and can be porous.^{17–20} Molecules can then diffuse through the pores in a manner similar to previous work on large area IETS structures with thin Al contacts (~50 nm).¹⁹ In particular, molecules in the presence of water vapor can penetrate the top metal of the completed tunnel junction more easily.^{17–20} A second possible mechanism, involves the deposition and diffusion of molecules from the exposed SiO₂ surface at the side edges of the tunnel junction. Furthermore, the use of SOI material raises the possibility of back gate control of the



FIG. 2. (Color online) Schematic diagram of a crossed Si NW/SiO₂/Al NW tunnel junction.

NW carrier concentration, and hence of the IETS characteristics.

III. MEASUREMENT

IETS measurements were performed at room temperature by using an Agilent 4155B parameter analyzer to obtain four terminal *I*–*V* characteristics (1000 measurement points). The *dI/dV*–*V* and d^2I/dV^2 –*V* characteristics were then calculated from the data. The noise floor in our *I*–*V* measurement was ~10 pA, allowing direct extraction of d^2I/dV^2 –*V* curves. Tunneling spectra were measured for NH₄OH, CH₃COOH, and C₃H₆O₂. Here, NH₄OH was deposited on the device by vapor treatment and CH₃COOH and C₃H₆O₂ by immersion. The four-terminal measurement circuit is shown in Fig. 4(a). Current was forced through the tunnel junction using terminals 2 (Al NW) and 1 (Si NW) and the voltage was measured between terminals 4 (Al NW) and 3 (Si NW).

A. Ammonium hydroxide (NH₄OH)

Electrical characteristics of a "clean" tunnel junction were measured first at 300 K. The dI/dV-V and d^2I/dV^2-V were then calculated numerically. As the device could not be immersed directly in ammonium hydroxide, vapor treatment is used to deposit NH₃ vapor molecules on the device. Here, the device was left in a petri dish in an ammonium hydroxide atmosphere for 2 h. Measurements were then repeated and compared to those from the clean device [Figs. 4(b)-4(d)]. It is possible to wash the device in acetone/isopropyl alcohol



FIG. 3. (a) Magnified SEM image of Si NW/SiO₂/Al NW tunnel junction and (b) SEM image of Si NW/SiO₂/Al NW tunnel junction widths.

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FIG. 4. (Color online) IET spectrum of NH₄OH on a Si NW/SiO₂/Al NW tunnel junction at 300 K (1000 measurement points, rectangles and circles used as marker to indicate different curves): (a) four-terminal measurement circuit, (b) the I-V characteristics of the tunnel junction before and after adsorption of NH₄OH molecules, (c) the dI/dV-V characteristics, and (d) the d^2I/dV^2-V characteristics of the device.

and recover the original clean measurement. This is in contrast to early IETS measurements where molecules were introduced during the tunnel junction fabrication.¹⁻⁴

Figure 4(b) illustrates the *I*–*V* characteristics of the tunnel junction before and after adsorption of NH₄OH molecules. Figure 4(c) displays the dI/dV–*V* characteristics, and Fig. 4(d) shows the d^2I/dV^2 –*V* characteristics of the device. The *I*–*V* characteristics [Fig. 4(b)] are diodelike, due to the presence of a Schottky barrier at the Si NW/SiO₂ interface. As we measure the data using a four-terminal measurement, this implies that the Schottky barrier must lie along the current path, i.e., at the interface and is not remote from the junction elsewhere in the Si NW (Fig. 5). The device current reduces slightly following NH₄OH treatment. In the d^2I/dV^2 –*V* characteristics [Fig. 4(d)], peaks are observed at ~–0.12 and –0.25 V (upper arrows). These may be attributed to the first and second excitation modes of an N–H bond at room temperature.

The lower arrows at ~ -0.15 and -0.3 V indicate previously reported excitation modes of N–H bonds in a MIM Al/Al₂O₃/Pb device at 4.2 K.²¹ The peaks in our data are shifted slightly relative to previous data. However, the peaks' separation remains the same at ~ -0.15 V.

shows the *I*-*V*, dI/dV-*V*, and d^2I/dV^2 -*V* characteristics,

respectively, for both the clean device, and the device



B. Acetic acid (CH₃COOH)

The IETS characteristics of a tunnel junction with acetic acid adsorption are shown in Fig. 6. Figures 6(a)-6(c)

FIG. 5. (Color online) (a) Inelastic tunneling forward bias, (b) inelastic tunneling reverse bias, and (c) IETS signals (The *I*–V characteristics, conductance G = dI/dV-V and IETS peaks d^2I/dV^2-V) for semiconductor/insulator/metal tunnel junction.



FIG. 6. (Color online) IET spectrum of CH₃COOH on a Si NW/SiO₂/Al NW tunnel junction at 300 K: (a) The *I*–*V* characteristics, for both the clean device, and the device with acetic acid adsorption. (b) The dl/dV–*V* characteristics, for both the clean device, and the device with acetic acid adsorption. (c) The d^2l/dV^2 –*V* characteristics, for both the clean device, for both the clean device, and the device with acetic acid adsorption. (c) The d^2l/dV^2 –*V* characteristics, for both the clean device, and the device with acetic acid adsorption. (Note: 1000 measurement points, rectangles and circles used as marker to indicate different curves.)

the clean device by immersion at room temperature for 5 min.

In a manner similar to the measurements of Fig. 4(b), the I-V characteristics are diodelike, both before and after immersion, and the device current reduces following immersion. The dI/dV-V characteristics of the device [Fig. 6(b)] show a reduction in conductance, and nonlinearities that correspond to the peaks in the d^2I/dV^2-V characteristics. In Fig. 6(c), the upper arrows indicate the measured peaks at \sim -0.25 and -0.75 V, which may be attributed to the first and third excitation modes of a C–H bond at room temperature. The lower arrows illustrate the previously reported excitation modes of C–H at \sim -0.36, -0.65, and -0.95 V in a

MIM device at 4.2 K.²² The peaks' separation in our measured data is ~ -0.5 V, which corresponds well to the separation between the first and third excitation modes of C–H bonds.

C. Propionic acid (C₃H₆O₂)

The IETS characteristics of a tunnel junction with $C_3H_6O_2$ adsorption are shown in Fig. 7. Figures 7(a)–7(c) shows the *I*–*V*, *dI/dV*–*V*, and d^2I/dV^2-V characteristics, respectively, for both the clean device, and the device with



FIG. 7. (Color online) IET spectrum of $C_3H_6O_2$ on a Si NW/SiO₂/Al NW tunnel junction at 300 K: (a) The *I*–*V* characteristics, for both the clean device, and the device with propionic acid adsorption. (b) The dI/dV–*V* characteristics, for both the clean device, and the device with propionic acid adsorption. (c) The d^2I/dV^2 –*V* characteristics, for both the clean device, and the device with acetic propionic adsorption. (Note: 1000 measurement points, rectangles and circles used as marker to indicate different curves.)

propionic acid adsorption. Propionic acid was adsorbed on the clean device by immersion at room temperature for 5 min.

In a manner similar to the measurements of Figs. 4(b) and 6(a), the *I*–*V* characteristics are diodelike, both before and after immersion, and the device current reduces following immersion. Figure 7(b), the dI/dV–*V* characteristics of the device, show a reduction in conductance and nonlinearities, which correspond to the peaks in the d^2I/dV^2 –*V* characteristics. In Fig. 7(c), the upper arrows illustrate measured peaks at ~–0.2, –0.5, and –0.85 V, which may be attributed to the first, second, and third excitation modes of a C–H bond at room temperature.

The lower arrows illustrate the previously reported excitation modes of C–H at \sim -0.36, -0.65, and -0.95 V in a MIM device at 4.2 K.²² The peaks' separation in our measured data is \sim -0.3 V, which corresponds well to the separation between the first and second and also between the second and third excitation modes of C–H bond.

IV. SUMMARY

IETS measurements are performed on Si NW/SiO₂/Al NW tunnel junctions at 300 K for NH₄OH, CH₃COOH, and C₃H₆O₂ molecules. The tunnel junction area is \sim 50 × 120 nm and tunneling occurs across the 10 nm thick SiO₂ layer. The *I*–*V*, *dI*/*dV*–*V*, and d^2I/dV^2 –*V* characteristics of the tunnel junction are measured before and after the adsorption of the NH₄OH, CH₃COOH, and C₃H₆O₂ molecules using vapor treatment or immersion. Peaks can be observed in the d^2I/dV^2 –*V* characteristics in all the cases following molecules adsorption. These peaks may be attributed

to the vibrational modes of N–H and C–H bonds. The peak separations are similar to previous reported work on micrometer scale MIM tunnel junction at low temperature.

- ¹R. C. Jaklevic and J. Lambe, Phys. Rev. Lett. 17, 1139 (1966).
- ²R. G. Keil, T. P. Graham, and K. P. Roenker, Appl. Spectrosc. **30**, 1 (1976).
- ³K. W. Hipps and U. Mazur, J. Phys. Chem. **97**, 7803 (1993).
- ⁴U. Mazur, X. D. Wang, and K. W. Hipps, Anal. Chem. 64, 1845 (1992).
- ⁵P. K. Hansma, *Tunneling Spectroscopy* (Plenum, New York, 1982).
- ⁶U. Mazur and K. W. Hipps, "Inelastic electron tunnelling spectroscopy," in *Handbook of Vibrational Spectroscopy*, edited by J. Chalmers and P.
- Griffiths (John Wiley and Sons Ltd, Chichester, 2002).
- ⁷V. Bommisetty, S. Bhandari, R. L. Karmacharya, D. A. Rislov, R. D. Mileham, and D. W. Galipeau, IEEE Sens. J. **8**, 983 (2008).
- ⁸D. G. Walmsley and J. L. Tomlin, Prog. Surf. Sci. 18, 247 (1985).
- ⁹B. C. Stipe, M. A. Rezaci, and W. Ho, Science **280**, 1732 (1998).
- ¹⁰Y. Sainoo, Y. Kim, T. Komeda, and M. Kawai, J. Chem. Phys. **120**, 7249 (2004).
- ¹¹N. Okabayashi, Y. Konda, and T. Komeda, Phys. Rev. Lett. **100**, 217801 (2008).
- ¹²J. G. Kushmerick, J. Lazorik, C. H. Patterson, R. Shashidhar, D. S. Seferos, and G. C. Bazan, Nano Lett. 4, 639 (2004).
- ¹³W. Wang, T. Lee, I. Kretzschmar, and M. A. Reed, Nano Lett. 4, 643 (2004).
- ¹⁴A. Agarwal, K. Buddharaju, I. K. Lao, N. Singh, N. Balasubramanian, and D. L. Kwong, Sens. Actuators, A 145, 207 (2008).
- ¹⁵E. Stern *et al.*, Nature **445**, 519 (2007).
- ¹⁶D. Wang, B. A. Sheriff, and J. R. Heath, Nano Lett. 6, 1096 (2006).
- ¹⁷W. J. Nelson, D. G. Walmsley, and J. M. Bell, Thin Solid Films **79**, 229 (1981).
- ¹⁸M. Higo, X. Lu, U. Mazur, and K. W. Hipps, Chem. Lett. **28**, 679 (1999).
 ¹⁹J. R. Bellingham, C. J. Adkins, and W. A. Phillips, Thin Solid Films **198**, 85 (1991).
- ²⁰K. W. Hipps and U. Mazur, J. Phys. Chem. **96**, 1160 (1992).
- ²¹G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand and Co., New York, 1945).
- ²²J. Lambe and R. C. Jaklevic, Phys. Rev. 165, 821 (1968).