

# A Combined SERS and MCBJ Study on Molecular Junctions on Silicon Chips

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**Abstract** — We have developed a combined Surface-enhanced raman spectroscopy (SERS) and mechanically controllable break junction (MCBJ) method to detect and characterize molecular junctions formed by two electrochemically nanofabricated electrodes on silicon chips. The method allows us to obtain vibrational spectra of the molecular junction and perform electron transport measurement on the molecules simultaneously. The preliminary I/V characterization and SERS measurement on an asymmetric molecule, OPE-NO<sub>2</sub>, and a symmetric molecule, OPE, were conducted. This approach may provide new insights into not only electron transport in molecules, but also the enhancement mechanism in single-molecule SERS.

**Keywords** — MCBJ, molecular junctions, conductance, single-molecule, SERS

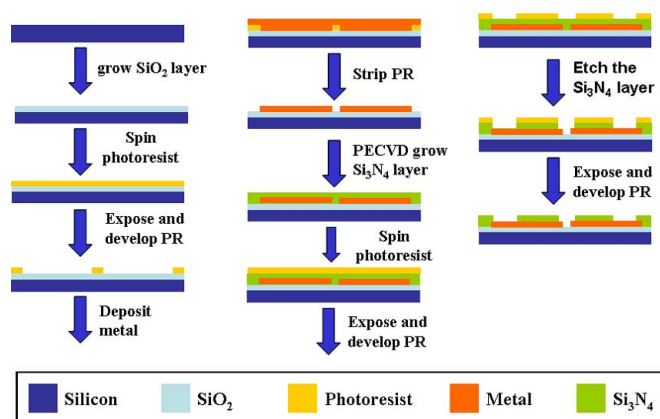
## I. BACKGROUND

Recently, molecular electronics and nanoelectronics devices have attracted great attention because of their potential application as key elements in future nanoelectronics and the fundamental interest of understanding the microscopic transport through a single molecule or small ensemble of molecules [1]-[5]. To date, many interesting molecular electron transport properties have been observed by some research groups, such as molecular transistors [6]-[7], conductance switching [8]-[9], rectification [10], and negative differential resistance (NDR) [11]-[13]. However, due to a lack of the direct information of molecular structure in the molecular junction, a good understanding of these properties is still a big challenge. Vibrational spectroscopies are capable of determining the chemical identity of a sample molecule and hence providing valuable structural information of the molecule. Inelastic tunneling spectroscopy (IETS) [14]-[16], Fourier transform infrared (FTIR) [17], and SERS [18]-[19] have been used to measure vibrational modes of molecules self-assembled on metal surfaces. However the IETS measures electron tunneling, which is powerful but requires cryogenic temperatures. The FTIR studies rely on multiple reflections with limited sensitivity. Very recently, SERS and surface-enhanced infrared spectroscopy (SEIRS) have been employed to characterize molecules within two metal plates at room temperature. But the measurements have been so far limited to large electrodes and a fix separation [18]-[19]. Recently, we developed a method that combines SERS and MCBJ to study the molecular junctions in the nanogap between two microelectrodes on a silicon chip [20]. As MCBJ can

continuously adjust the gap between two electrodes very precisely, we can maximize the SERS activity by simply tuning the gap to a suitable width in order to probe the molecules wired to two electrodes during the electrical measurement. This approach has at least three benefits: First, the MCBJ allows us to precisely and stably adjust the separation between the electrodes on a silicon chip over a range from a few angstroms to about nanometers with a resolution of sub-Å [21]-[22]. The junction formed by the electrode pairs can be considered as a nanoparticle dimer with a controllable gap width for the SERS study. Second, building molecular devices also highly demands an ultrasensitive spectroscopic method that can directly characterize single molecules connected to two electrodes at room temperature. Third, SERS is a very sensitive method to detect the adsorption modes and orientations of molecules in the nanogap with the change of the microscopic environment around the molecules.

## II. EXPERIMENT RESULTS AND DISCUSSION

The original electrodes pairs are fabricated following the conventional optical lithography procedure, as show in scheme 1. The key parameters of the lithography process are: both the thicknesses of silicon oxide layer and the Si<sub>3</sub>N<sub>4</sub> cover layer are 200 nm; the thickness of Au metal layer is 50 nm with 5 nm Ti adhesion layer underneath; the separation of the electrode pair is about 1 μm (Fig. 1a). We used



Scheme 1 optical-lithography process for fabricate the original electrodes pair

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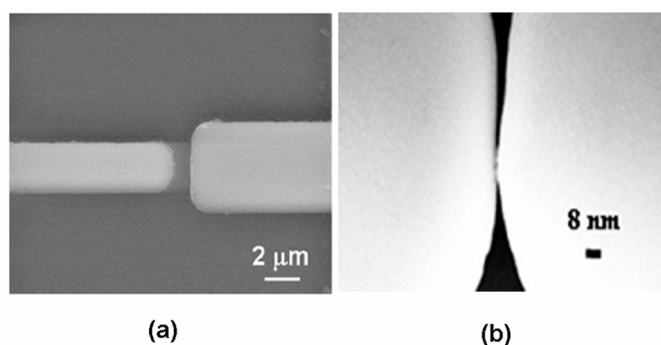


Fig. 1 SEM images of a) the original electrodes pair separated about 1  $\mu\text{m}$ ; b) the electrodes pair separated about 1.5 angstrom after electrodeposition (out of the resolution of our SEM, calculated from tunneling current).

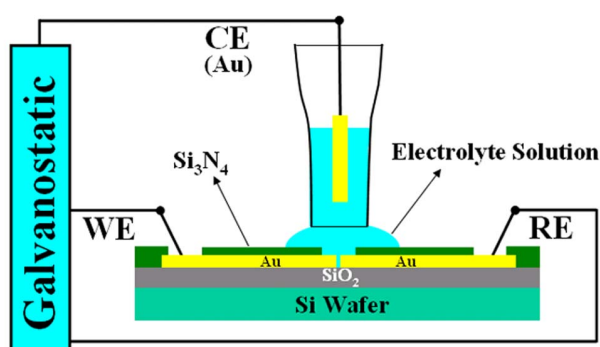


Fig. 2 Schematic drawing of the experimental setup

electrodeposition to reduce the width of the gap to form an Au nanojunction. In comparison with previous methods, our new electrodeposition method has two major differences, namely, the electrode configuration and the feedback mode (Fig. 2) [23]. Before electrodeposition, the device was first cleaned by piranha solution for 10 seconds, then rinsed with pure water and ethanol, and finally dried with Ar gas. (Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care.) We then electrochemically deposited Au over the pair of electrodes to obtain electrode pairs connected or with a gap of several angstroms (Fig. 1b). We can get electrodes pairs with a separation width from a few angstroms or even connected to several nanometers by controlling the potential feedback during the electrodeposition process. The chip was then mounted on the MCBJ setup using a piezoelectric transducer to control the open and close of the two Au electrodes with sub- $\text{\AA}$  resolution [24]. The gap width is estimated and controlled by monitoring the tunneling current obtained with a semiconductor characterization system (Keithley 4200) based on the formula  $I = (2e^2/h)V\exp(-\beta d)$ , where  $I$  is the tunnel current between the electrodes gap,  $e$  is the mass of the electron,  $h$  is the planck constant,  $V$  is the applied bias,  $\beta$  is the decay constant, and  $d$  is the gap width. Before assembling molecules inside the gap, we did control experiments to determine the gap width when the piezo was set at different position. As the separation between the two electrodes is linearly related to the displacement of piezo along the vertical direction, we can even extrapolate the separation between electrodes when they are out of the tunneling region. During the SERS

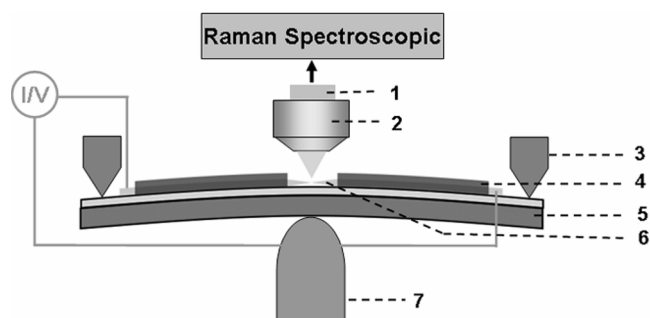


Fig. 3 Schematic drawing of the experimental setup of combined SERS and MCBJ. 1 – laser beam, 2 – lens, 3 – counter support, 4 –  $\text{Si}_3\text{N}_4$  cover layer, 5 – bending beam, 6 – Au electrode, 7 – piezo.

measurement, the incident laser was focused onto the molecular junction via a microscope objective ( $\times 50$ ,  $\text{NA} = 0.55$ ) from the top of the MCBJ chip, and the scattered light was collected with the same objective and directed to a Raman confocal spectroscopic (LabRam I, Jobin Yvon) as shown in Fig. 3. The SERS and electrical measurement can be done simultaneously.

We started the electrical measurement by adjusting the gap to a width of 1-2 nm. A droplet of solution containing probe molecules was placed over the gap to allow the molecules to be adsorbed onto the electrodes. Then the solution was allowed to dry in air for 30 min, which should be sufficiently long for a complete evaporation of the solvent, especially for the highly volatile solvent. Afterwards, the piezo was withdrew step by step, which brought the two electrodes close to each other leading to an increase of the tunneling current. We can then easily create molecular junctions by closing and re-opening the two electrodes repeatedly. Fig. 4 shows a typical I/V curve for a conjugated asymmetric molecule, OPE- $\text{NO}_2$ , the chemical structure of which is shown in the inset of Fig. 4. In Fig. 4, the black line represents the tunnel current of the nanogap without molecules, and the red line represents the I/V curve of nitro-substituted oligo(phenylene ethynylene) (OPE- $\text{NO}_2$ ) molecules bridged over the nanogap, formed a gold/OPE- $\text{NO}_2$ /gold sandwich structure. When the probe molecules are bridged over the nanogap, the resistance will

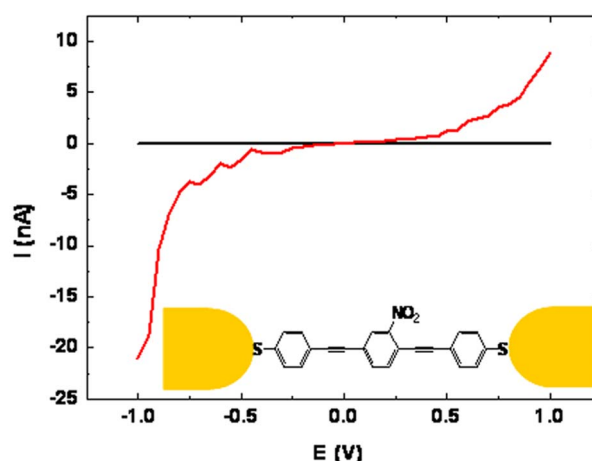


Fig. 4 I/V curve characterization of Au/OPE- $\text{NO}_2$ /Au molecular junctions.

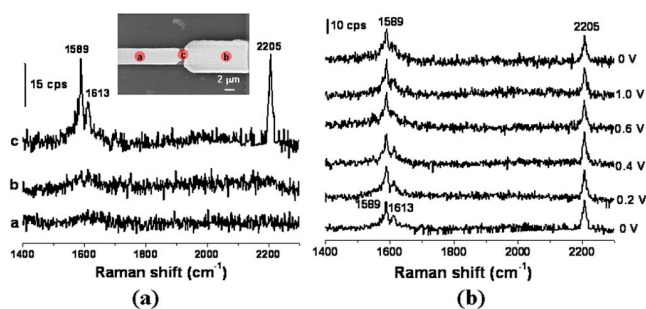


Fig. 5 a) SER spectra of OPE-NO<sub>2</sub> on electrodes surface (a,b) and in the gap (c), the inset is the top view of a pair of gold electrodes, the red solid circles represent laser spot ; b) SER spectra of OPE-NO<sub>2</sub> in the nanogap with different applied voltages, laser: 632.8 nm.

drop at about 3 orders of magnitude as compared with the case without the molecules. The value of resistance of the molecule is about  $7.0 \times 10^8 \Omega$  calculated from the I/V curve near the zero bias, which is very close to the reported value [25]. From Fig. 4, we also found that the asymmetric molecule has an asymmetric I/V curve, which is also similar to the result of J. Reichert et al. [26]. The SERS measurement was made at different positions of the electrodes, such as the center and the edge of the electrode and in the gap (see in the inset of Fig. 5a). Since the electrodeposited layer is rather smooth even on the nanometer scale, see the inset of Fig. 5a, the SERS signals of probe molecule from such a surface are very weak (lines “a” and “b”). In contrast, the signal from the gap is much stronger than that from other areas (line “c”). We also found that the SERS intensity of the sample molecules depends critically on the incident light polarization and the gap width. When the incident laser is polarized along the long axis of the two electrodes, the SERS signal obtained in the nanogap is the strongest, when the polarization direction is perpendicular to the long axis of the two electrodes, the SERS intensity decreases dramatically, which confirms that the SERS signal is mainly contributed by the molecules lodged inside the gap [20]. For the OPE-NO<sub>2</sub> molecular junction, there are four prominent peaks in the SER spectrum at 1589, 1613 and 2205 cm<sup>-1</sup> (Fig. 5a). We assign the peaks at 1589 cm<sup>-1</sup> and 1613 cm<sup>-1</sup>

<sup>1</sup> to the phenyl ring C=C stretching vibrations ( $\nu_{8a}$ ), and the peak at 2205 cm<sup>-1</sup> to the C≡C stretching vibration. Then, the voltage applied on the molecular junction was varied from 0 V to 1.0 V and then brought back to 0 V (Fig. 5b). The SERS measurement was made at the same time while the applied voltage was on. As can be seen in Fig. 5b, that the intensity and frequency of bands did not show observable change with the applied voltage.

Fig. 6 gives the representative I/V curve and the numerically differentiated data dI/dU of a similar molecule, unsubstituted oligo(phenylene ethynylene) (OPE), the chemical structure of which is shown in the inset of Fig. 6. From the I/V curve, we found that the symmetric molecule has a symmetric I/V curve and the resistance of the OPE molecule is about  $3.0 \times 10^9 \Omega$  calculated at near the zero bias. This value is almost one order magnitude larger than the previous report using STM break junction method [25]. This difference may be due to the different microscopic details of the molecule-metal contacts and the different microscopic environment around the molecules in the nanogap. For the SERS measurement, we obtained a similar result to the OPE-NO<sub>2</sub> that the intensity and frequency of bands did not show observable change with the applied voltage. Similar phenomenon has also been found by other group [19] and in our experiments of some other molecules. The reason of the phenomenon is still under investigation in our laboratory.

### III. CONCLUSION

In summary, we have performed the conductance and SERS measurements through a metal/OPE-NO<sub>2</sub>/metal and metal/OPE/metal molecular junctions with the SERS-MCBJ combined method. From the I/V curves, we found that the asymmetric molecule has an asymmetric I/V curve and the symmetric molecule has a symmetric I/V curve. The resistances estimated from the I/V curve for OPE-NO<sub>2</sub> is very close to the reported value, whereas for OPE molecule is about one order magnitude larger than the reported value. This difference may be due to the different microscopic details of the molecule-metal contacts and the different microscopic environment around the molecules in the nanogap. Although the reproducibility is still low at the present stage and there are still some phenomena are unclear, we believe that this combination of SERS and MCBJ method will be developed into a useful tool to characterize molecules in molecular junctions and thus contribute to a better understanding of electron transport in molecules and the mechanism of single-molecule SERS generated from nanoparticle junctions.

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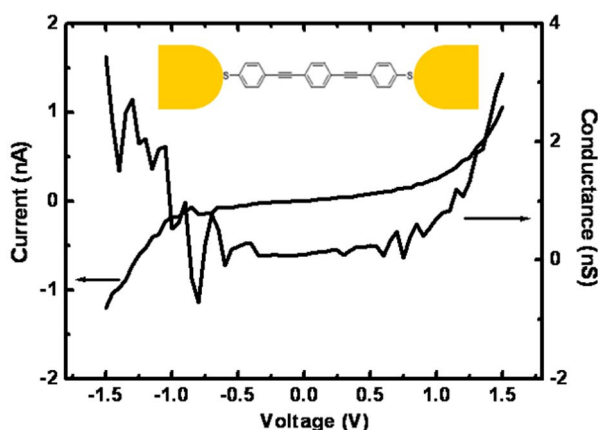


Fig. 6 Representative I/V curve and the numerically differentiated data dI/dU (conductance) of the Au/OPE/Au molecular junctions.

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