Charge transport across metal molecule interfaces probed by BEEM

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Abstract. We use Ballistic Electron Emission Microscopy (BEEM) technique to determine directly the Schottky barrier distribution over silver /H-T₃-(CH₂)₄-HS (abbreviated as T3C4SH) self assembled monolayer interface area with nanometer scale spatial resolution. The self-assembled monolayer is absorbed on template stripped gold. BEEM images show spatially non-uniform carrier injection. A Wentzel Kramel Brillouin (WKB) calculation is performed and compared with BEEM spectra. The results show that the measured currents are four orders of magnitude larger than the direct tunnelling contribution, indicating molecular levels being accessed. To further substantiate the findings, characterization by STM distance versus potential spectroscopy is carried out to determine injection barriers at the interface. The results from these two techniques are compared and the implications of which will be discussed.

1. Introduction

With organic semiconducting materials reaching the early stages of commercialization, charge transport across metal-molecule interfaces is generally acknowledged to be one of the important parameters for device operation. Such studies can elucidate the underlying physics of Schottky barrier formation, a matter of considerable controversy for metal-inorganic semiconductor interfaces. Self-assembled monolayers (SAMs) have highly organized surface structures with uniform density of terminal functional groups and have become a focus of intense interest with the discovery that electronic devices can be fabricated using SAMs with deposited metal contacts. This method yields a vertical device configuration.

In this paper, we use a variant of STM (Scanning Tunneling Microscopy) i.e. ballistic electron emission microscopy (BEEM) and spectroscopy (BEES) to measure the charge transport across the interface of silver/terthiophene-5-yl-butan-1thiol (T3C4SH) immobilized on mica template stripped Au(111) film. BEEM technique allows us to determine the distribution of Schottky barrier (SB) over the interface area with nanometer scale spatial resolution, unlike conventional spectroscopy and current-voltage measurements that average over millimeter areas. The results are compared with the Wentzel Kramers Brillouin (WKB) model to discuss the effect of tunneling contribution in the measurement. We also show characterization by STM distance versus potential (z-V) spectroscopy [1] to probe directly the injection energies for electrons and holes into polaronic states (E_p- and E_p+) of the...
organic material from which the polaron energy gap is calculated. The injection barriers at the organic/gold interface, deduced from these measurements, will be discussed.

The configuration of a BEEM experiment is shown schematically below. The tip injects a highly collimated beam of ballistic carriers into the top metal film (Ag in this case), which cross over into the molecule or semiconductor (T3C4SH in this case) if their energies exceed the local band offset or Schottky barrier.

![Figure 1. Schematic diagram of BEEM set-up.](image)

In the imaging mode, the tunneling current is maintained constant as a function of tip position at fixed bias and the BEEM collector current is recorded as a function of tip position concurrently. STM topography and BEEM images are then obtained. In the spectroscopy mode, the collector current is measured as a function of tip bias at a fixed location and constant tunnel current to produce the BEEM I-V spectra.

2. Results and discussion

We first show the STM image of the T3C4SH molecule self-assembled on template stripped gold (figure 2). The scan area and topography full scale on this image is approximately 220 nm and 4 nm respectively. The second STM image shows the topography of the 10 nm thick Ag film deposited at 77 K on the self assembled molecular layer, over a comparable area. The film is nominally 8 nm thick. It should be noted that these two STM images are only representative, and do not correspond to identical areas of the sample. This is an experimental limitation. The grain size of the Ag film cannot be determined. Our earlier work showed that Ag forms approximately 10 nm grains when evaporated onto cold substrates. The topography scale on this image is 2 nm. The last panel shows a BEEM current image. The bias on the STM tip is 0.6 V and the tunneling current is 2 nA. The full scale current on the BEEM image is 8 pA.

![Figure 2.](image)

The BEEM current image indicates a non-uniform transparency of the interface with bright spots that range in size from a few nanometres to about 20 nm. BEEM current directly measures the conductance of the interface as it quantifies the number of carriers being collected at the bottom
electrode; at a fixed voltage that is applied to the STM tip. An averaged BEEM spectroscopy of the interface taken at the bright and dark region of the BEEM image is shown in Figure 3. Approximately 30 individual spectra, acquired over different locations within a nominally 5 nm square, are averaged to improve the signal to noise ratio.

The BEEM spectra over the bright regions as well as the dark regions indicate a Schottky barrier of 0.5 V. We note that this is the injection barrier for holes, since the sign of the bias on the STM tip is positive. Considering the fact that the oxidation potential for this molecule is 0.5 V, when measured relative to Ag [2], the agreement is indeed satisfactory. These results demonstrate the utility of the BEEM technique: no other technique is capable of giving a pictorial representation of charge transport across the metal-molecule interface with nanometer scale resolution.

In this experiment, we have two metal films separated by a molecular layer that is approximately 1.5 nm thick. Direct tunneling from one metal electrode to the other is a possibility that needs to be considered. Direct tunneling would make the results of this work open to question. In order to ensure that the measured collector current is not influenced by tunneling, we carried out a calculation within the framework of the WKB approximation for tunneling from silver through a potential barrier to gold, and compared with the BEEM results [3]. The parameters were taken based on the assumptions that T3C4SH is a 1.5 nm long tunneling barrier. The work functions for Ag and Au are 4.26 and 5.1 eV as taken from published literature [4]. The calculated I–V data from the model for a 10 nm square region is shown in Figure 4.

The chosen dimensions for the junction are rough estimates of the spreading area in the metal base by ballistic charge carriers due to mutual repulsion. It should be noted that the tunneling current contribution is four orders of magnitude smaller than the BEEM current. It should be noted that tunneling does not require the charge carriers to access the molecular electronic energy levels. The only possible explanation for this discrepancy is that our BEEM experiment actually accesses the

Figure 3. Average of 30 BEEM spectra of Ag/T3C4SH on Au at bright and dark region of BEEM image.

Figure 4. I–V tunneling spectroscopy of Ag/T3C4SH on Au obtained by WKB modeling for a 10 nm square area.
molecular energy levels, and therefore the collector current is higher than anticipated. This is similar to the device configuration of a resonant tunneling diode. Resonant tunneling currents are typically much higher than direct tunneling currents [5]. Therefore we can be confident that molecular levels are being accessed.

Additionally, the STM distance versus potential spectra are carried out at room temperature under atmospheric pressure using platinum iridium tip on T3C4SH/Au sample. In this STM-based technique, the z-V curve probes the density of states via the voltage dependent tip displacement at constant tunneling current. By reducing the voltage, the tip is brought to close proximity and finally direct physical contact with the molecules. At a characteristic threshold bias voltage, the conduction mechanism for the carriers favors direct tunneling to the gold substrate rather than through the T3C4SH molecules. This transition is observed by a significant change of the slope in the z-V curve. Figure 5 shows the z-V spectrum of T3C4SH on Au. For this measurement, the bias voltage is ramped with decreasing magnitude for each polarity. The thin red lines show the linear interpolation from the two distinct slopes of averaged spectrum (shown by thick brown line). The intersection of these lines determines the values of electron and hole threshold voltages.

The z-V spectra are obtained at different areas and on several similar samples as tabulated below. The statistical average polaron energy gap \( E_{\text{gap}} \) yields \( 4.7 \pm 0.5 \) eV. From the analysis of the spectra, we also deduce the electron and hole-injection threshold energies for T3C4SH to be approximately \( 2.4 \pm 0.1 \) eV and \( 2.3 \pm 0.5 \) eV respectively.

**Table 1.** Values of injection energies for electrons and holes into polaronic states of T3C4SH acquired at different locations and samples and their corresponding threshold energies \( (E_e, E_h) \) and charge injection gap.

| \( E_{p+} \) (eV) | \( E_e \) (eV) | \( E_{p-} \) (eV) | \( E_h \) (eV) | \( E_{\text{gap}} \) (eV) | Charge injection gap (eV) |
|----------------|-------|----------------|-------|----------------|----------------|
| -2.4           | 2.2   | -2.4           | 2.8   | 4.6            | 5.2            |
| -2.4           | 2.4 ± 0.1 | 1.9 | 2.3 ± 0.5 | 4.3            | 4.7 ± 0.5      |
| -2.4           | 2.3   | -2.4           | 2.3   |               | 4.7            |

Figure 6 presents the summary of the results for the interface between silver/T3C4SH on template stripped gold. As the SAM molecule comprises two segments, that is, \( \alpha \)-functionalized terthiophene (T3) with alkanethiol (C4SH) anchoring groups, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of individual segment are depicted in the schematic diagram. In the figure, the charge injection from silver into terthiophene gives a barrier of 0.5 eV as probed using BEEM technique, which is shown by the dash circle. The hole and electron injection
barriers of the anchoring molecule with respect to the Fermi level of template stripped gold as obtained using STM z-V technique are each found to be $2.4 \pm 0.1$ eV and $2.3 \pm 0.5$ eV as indicated by the dotted circle.

STM z-V technique has been applied to some organic films of a few nanometers thick on gold surface [6,7]. However, in this study the SAMs are bonded directly to Au atoms via the thiol group. Thus, a series of dipoles is induced upon adsorption as the charge rearrangement upon SAM formation rapidly decays in both the metal and the SAM. It leads to the potential step across the S-Au bonding region [8]. It is unclear whether the covalent bond influences the injection threshold value. The results position the HOMO level well below the Fermi level of the gold substrate.

**Figure 6.** Schematic diagram of energy band structure of metal molecule contact. Since the SAM consists of two segments, i.e. terthiophene and alkanethiol, each HOMO and LUMO level is drawn separately. Dash and dotted circles indicate the injection barrier of Ag/SAM and SAM/Au interfaces obtained using BEEM and STM z-V techniques respectively. Not drawn to scale.

### 3. Conclusion

We demonstrate that BEEM can be used for high-resolution studies of metal/SAM interface. Nanometre resolution imaging of the interface shows non-uniform charge injection across Ag/T3C4SH-on-Au. A WKB calculation indicates that the tunnelling contribution is insignificant and measured BEEM current arises from injected carriers accessing molecular levels. We also applied the STM z-V technique to determine the injection barriers at the interface of SAM. The results show the position of HOMO level well below the gold Fermi level, likely attributed to localized charge fluctuations at the metal-molecule interface induced by the covalent bond formation. At present we are not sure what happens at the interface between T3 and C4SH molecular segments. Further studies need to be done on the interface of each segment of molecule as separate entity with metal substrate to conclude the findings.

### References

[1] Muller P, Alvarado SF, Rossi L and Rieb W 2001 *Mater. Phys. Mech.* 4 76
[2] Bauerle P (private communication)
[3] Simmons JG 1963 *J. Appl. Phys.* 34 1793
[4] Michaelson H.B. *J. Appl. Phys.* 48 4729
[5] Datta S 1995 Cambridge University Press, Cambridge
[6] Alvarado SF, Rossi L, Muller P, Rieb W 2001 *Synth. Met.* 122 73
[7] Alvarado SF, Seidler PF, Lidzey DG and Bradley DDC 1998 *Phys. Rev. Lett.* 81 1082
[8] Heimel G, Romaner L, Bredas JL and Zojer E 2006 *Phys. Rev. Lett.* 96 196806