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Ballistic electron and hole transport through individual molecules

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Abstract. Recently the ballistic transport through organic molecules could be analyzed with submolecular resolution by an extension of ballistic electron emission microscopy. In this work we compare the results of ballistic transport of electrons and holes through C\textsubscript{60} molecules deposited onto a Bismuth/Silicon Schottky diode. The study of hole transmission also exhibits molecular a resolved pattern in the transmission images showing the molecular periodicity of the C\textsubscript{60} layer.

1. Introduction

The ongoing development of molecular-based semiconducting devices requires a detailed understanding of charge transport e.g. through organic molecules. In order to extend the lifetime of an electronic device it is necessary to reduce the power dissipation within the device. This may be done, e.g. through the concept of a ballistic electron transistor [1]. In the case of ballistic transport no energy is dissipated and high speed switching processes with a minimal energy loss can be realized. For the ballistic transport of charge carriers through molecules, both the transport of electrons and the transport of holes are important.

Ballistic electron emission microscopy (BEEM), a extension of scanning tunneling microscopy (STM) [2], is not only a powerful tool to analyze the buried interfaces of metal/semiconductor Schottky diodes, but also is offers the possibility to study the electric coupling of molecules adsorbed on top of the metal layer [3]. In addition to the detection of electrons the BEEM method may also be used to study the transport of holes [4].

To perform BEEM a thin metallic layer is deposited onto a semiconducting substrate. At the interface between these materials a Schottky barrier is formed. A tip of a scanning tunneling microscope is used to inject charge carriers into the metal layer. If the metal layer and the semiconductor are contacted separately the fraction of ballistic electrons which propagate through the metal film and overcome the Schottky barrier can be measured independently of the total tunneling current. The charge carriers to be analyzed may be electrons or holes, depending on the doping of the semiconducting substrate. If the semiconductor is n-doped the combination of metal and semiconductor leads to a barrier for electrons in the case of p-doping for holes. In most cases BEEM

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studies mainly focused on the analysis of metal/semiconductor interfaces. A few BEEM studies were extended to study the ballistic transport across a metal/semiconductor interface if organic material was deposited in between the metal layer and the semiconducting substrate [5, 6]. Also the theoretical work focuses on the ballistic transport through molecules placed at the interface between semiconductor and topping electrode [7].

In our group it was demonstrated that the coupling of molecules to a metallic substrate may be analyzed using BEEM, if the molecules to be studied are placed on top of the metallic layer of a metal/semiconductor Schottky device [3]. To study the transport of electrons the electrons were injected from the tunneling tip into the empty states of the C\textsubscript{60} molecules. The subject of the present paper is the analysis of the transport of holes through an organic layer involving the occupied states of molecules and their influence to the charge transport. A scheme of the experimental setup for both cases, electron and hole transport, is shown in figure 1.

![Figure 1. Scheme of the BEEM setup. One tip ensures a separated electric contact to the Bi-film, while the second STM tip injects electrons or holes depending on the substrate doping (n-type or p-type) and the bias voltage (negative or positive).](image)

2. Experiments and Discussion

The BEEM experiments were carried out using a modified Omicron Nanoprobe multi tip STM system providing true atomic resolution on each STM stage at a base pressure of 2x10\textsuperscript{-10} mbar. As a substrate p- and n-doped Si(100) single crystals were used. In both cases the Silicon substrates were cleaned by HF-etching before transferring it into the UHV chamber. Afterwards the Silicon single crystals were further cleaned by cycles of flashing up to 1500K in order to get rid of the hydrogen passivation and any other adsorbates. Then 3nm of Bismuth were deposited at a low temperature of 150K analogue to the preparation described elsewhere [8, 9, 10]. The result is a flat Bi film, as well on the p-doped as on the n-doped Si(100). The C\textsubscript{60} was deposited onto the Bi-surface at room temperature. All BEEM measurements were carried out at 150K in order to increase the rectifying behavior of the Schottky diode. To avoid any photo current affecting the measurements all BEEM studies have to be carried out in complete darkness. To ensure a separate electric contact to the Bi-film, one STM unit was equipped with a gold tip which then was gently pressed into the Bismuth layer. It is connected to ground potential (figure 1). In order to perform BEEM, the Si substrate was highly doped at the backside to provide an Ohmic contact. The resulting BEEM current of ballistically transmitted electrons or holes was detected using a current to voltage amplifier with a cut off frequency of 300Hz and amplification of 10\textsuperscript{10}V/A. The total tunneling current was detected using a current to voltage amplifier with a cut off frequency of 7 kHz and a gain of 10\textsuperscript{9}V/A [11].

On an n-doped Si-substrate the flow of electrons was studied which were injected either directly into the Bismuth layer or via a layer of C\textsubscript{60} molecules deposited on top of the Bi film. At a coverage of about half a monolayer, the C\textsubscript{60} form triangular shaped islands which exhibit a hexagonal ordering of the molecules comparable to C\textsubscript{60} on Au(111) studied by Altman and Colton [12]. For the C\textsubscript{60} covered areas an attenuation of the BEEM current of a factor of about 8 can be clearly seen (figure 2).
In addition, the BEEM images reveal a submolecular pattern which is rather different from the molecular corrugation observed in the topography [3]. At energies between the Schottky barrier height of the Bi/Si interface of about -0.6eV and an injection energy of -1.6eV the molecules seem to have a homogeneous transmission of ballistic electrons across one molecule, while between the molecules the ballistic current is attenuated. In contrast, at energies greater than -1.6eV the appearance of the C$_{60}$ molecules changes within the BEEM images. This effect could be attributed to the LUMO+1 state of the C$_{60}$ molecules and the influence of increased transport probability at the edges of the C$_{60}$ molecules. The contrast in the BEEM current is rather strong even if the C$_{60}$ molecules are not well resolved within the topographic image.

Figure 3 shows in comparison the findings for holes, by using a p-doped Si substrate and a positively biased STM tip. This allows accessing the influence of the HOMO states of the molecular layer to the ballistic transport through the C$_{60}$/Bi/Si heterostructure. Figure 3 displays a topographic overview of the partially C$_{60}$ covered sample as well as the corresponding BEEM image of the same area.

As for the electron transport, also the transmission of ballistic holes is decreased across the molecular layer in comparison to the bare Bismuth film on the left side of the image (figure 3b). A closer inspection of the C$_{60}$ covered area reveals a monolayer coverage of C$_{60}$ in the lower middle of figure 3a (y), and also on the right side of the image (z). The height difference of the molecular layers is due to a step of the underlying Bi surface. The overall BEEM current is reduced by about 70% for
the C\textsubscript{60} covered areas. At the position of each single molecule the current is attenuated while in between the molecules in the middle of each C\textsubscript{60} trimer, a increase of the BEEM current is visible. In addition some C\textsubscript{60} molecules seem to have a higher transmission than average. In the topographic image these molecules appear somewhat lower. This could be due to the orientation of the C\textsubscript{60} relative to the substrate. This means that these molecules could face the Bi surface with a pentagon instead of a hexagon resulting in a lower appearance of the molecule as reported e.g. for NC-AFM measurements of C\textsubscript{60} on KBr [13]. In the view of these aspects in the case for a higher transmitting C\textsubscript{60} the tunneling tip is closer to the Bismuth surface, so that the outcome of ballistic electrons may be somewhat higher.

Figure 4 shows linescans across a row of C\textsubscript{60} molecules for both the topography and the BEEM image. It can be seen, that the corrugation of the BEEM current is reversed in comparison to the topographic appearance. This kind of anticorrugation has already been seen for the system of CoSi\textsubscript{2}/Si(111) [14, 15]. However, we suggest that the contrast results from the variation of the distance between the injecting tip and the Bismuth surface. Across the molecules the distance between the tip and the Bismuth layer rises up to the center, so that the distance to the Bi surface is increased leading to a lower outcome of ballistic holes. Otherwise in between the molecules the distance reaches a minimum resulting in a rise of the ballistic current. In contrast to the transport of electrons it seems that the electronic states of the C\textsubscript{60} molecules do not contribute significantly to the transmission of ballistic holes at the given injection energy.

3. Summary

We have reported on the transport of ballistic charge carriers through an organic layer of C\textsubscript{60} molecules. The flux of ballistic electrons through the molecular covered areas is reduced by the molecular adlayer. In contrast to the transport of electrons, for holes the BEEM current images show a correlation of the BEEM signal and the topography. This results in a reduction of the BEEM current across the molecular layer with triangularly shaped high transmission spots. Due to a slight height modulation of the C\textsubscript{60} molecules, some molecules exhibit a higher BEEM signal, as the BEEM current depends on the height difference between the injecting tunneling tip and the Bismuth surface. We have shown that the BEEM geometry presented in [3] can also be applied to analyse the transport of holes through organic adsorbates with high lateral resolution. This opens the possibility to analyze the occupied states of molecular adsorbates and their influence on the ballistic transport.

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References

[1] Timp G, et al., *IEDM Tech. Dig.*, 55 (1999)
[2] Kaiser W J and Bell L D, *Physical Review Letters* 60, 1406 (1988)
[3] Bannani A, Bobisch C, Moeller R, *Science* 315, 1824 (2007)
[4] Bell L D, H Hecht M, Kaiser W J, *Physical Review Letters* 64, 2679 (1990)
[5] Troade C, Jie D, Kunardi L, O'Shea S J, Chandrasekhar N, *Nanotechnology* 15, 1818 (2004)
[6] Özcən S, et al., *Applied Physics Letter* 90, 092107 (2007)
[7] Kirezenow G, *Physical Review B* 75, 045428 (2007)
[8] Bobisch C, Bannani A, Matena M, Moeller R, *Nanotechnology* 18, 055606 (2007).
[9] Jnawali G, Hattab H, Krenzer B, Horn von Hoegen M *Physical Review B* 74, 195340 (2006)
[10] Krenzer B, et al., *New Journal of Physics* 8, 190 (2006)
[11] all current to voltage amplifiers were constructed by Detlef Utzat
[12] Altmann E I and Colton R J, *Physical Review B* 48, 18244 (1993)
[13] Burke S A, Mativetsky J M, Hoffmann R, Grütter P, *Physical Review Letters* 94, 096102 (2005)
[14] Sirringhaus H, Lee E Y, von Kaenel H, *Surface Science* 331-333, 1277 (1995)
[15] Reuter K, et al., *Physical Review Letters* 81, 4963 (1998)