Ballistic Electron Emission Microscopy/Spectroscopy on Au/Titanylphthalocyanine/GaAs Heterostructures

S. Özcan[1], T. Roch[1], G. Strasser[1], J. Smoliner[1], R. Franke[2] ,T. Fritz[2]

[1] Institut für Festkörperelektronik, TU Wien, A-1040 Vienna

[2] Institut für Festkörperphysik, TU Wien, A-1040 Vienna

In this article Au/titanylphthalocyanine/GaAs diodes incorporating ultra smooth thin films of the archetypal organic semiconductor titanylphthalocyanine (TiOPc) were investigated by Ballistic Electron Emission Microscopy/Spectroscopy (BEEM/S). Analyzing the BEEM spectra, we find that the TiOPc increases the BEEM threshold voltage compared to reference Au/GaAs diodes. From BEEM images taken we conclude that our molecular beam epitaxial (MBE) grown samples show very homogeneous transmission, compared to wet chemically manufactured organic films. The barrier height measured on the Au- TiOPc-GaAs is $Vb \sim 1.2eV$, which is in good agreement with the data found in reference [1]. The results indicate that TiOPc functions as a p-type semiconductor, which is plausible since the measurements were carried out in air [2].

Introduction

In recent years, organic semiconductors have attracted much interest due to their variety of interesting optical, electrical and photoelectric properties. Photo- and electro-active organic materials have been the subject of recent attention including organic semiconductors, organic light emitting diodes [3], [4], organic field effect transistors [5], [6], or photovoltaic devices [7], [8]. In addition, organic semiconductors are already widely used in xerography, plate making printings and laser printers. Physicists and chemists have focused on the charge transfer phenomena of organic molecules and polymer organic semiconductors in the field of organic solar cells during the past decade. Besides these applied aspects there are important features motivating basic research, namely the interface properties between semiconductors and organic films, e.g. the deformation of the bandstructure at the interface.

Experimental

Ballistic-electron-emission microscopy (BEEM) [9], [10] is a three terminal extension of scanning tunneling microscopy (STM) [11], [12], where electrons tunnel between the STM tip and a thin Au film evaporated on a semiconductor surface such as Si or GaAs. If the electron energy is high enough to overcome the Schottky barrier height at the metal-semiconductor interface the electrons can penetrate ballistically into the semiconductor. This causes a current, which is measured with the third electrode on the backside of the sample. By sweeping the applied tip voltage BEEM current spectra can be obtained. By mapping the BEEM current for a constant tip bias while scanning the sample surface, images can be taken with a spatial resolution of about 1 nm. Over the last two decades BEEM became a well-established technique to determine Schottky

barrier heights (SBH) and subsurface band offsets. An overview of this technique can be found in detail [13] – [15]. To guarantee good internal sample resistance and optimized BEEM signals, molecular beam epitaxial (MBE) grown GaAs samples were used as substrates. In detail, low doped ($ND \sim 1 \times 10^{16}$ cm^{-3}) GaAs layers ($d \sim 1\mu$m) were grown on an $n+$-wafer. On these substrates, TiOPc-films ($d \sim 6$ monolayers) were grown with organic MBE. Finally, a 7 nm Au layer was evaporated on top of it.

Results and Discussion

Figure 1(a) shows the topographic STM image and Fig. 1(b) the corresponding BEEM image of our Au/TiOPc/GaAs sample. The BEEM image was obtained simultaneously at a tip bias (V_t) of 1.4 V and a tip current (I_t) of 5 nA, with a scan area of 500 nm x 500 nm. The STM constant current image shows the typical or characteristic granular structure of Au. In the corresponding BEEM image, brighter areas indicate an enhanced electron transmission. Features visible in the BEEM image correlate exclusively with the granular structure and the topographic features of the Au-film and can not be correlated to the organic film underneath.
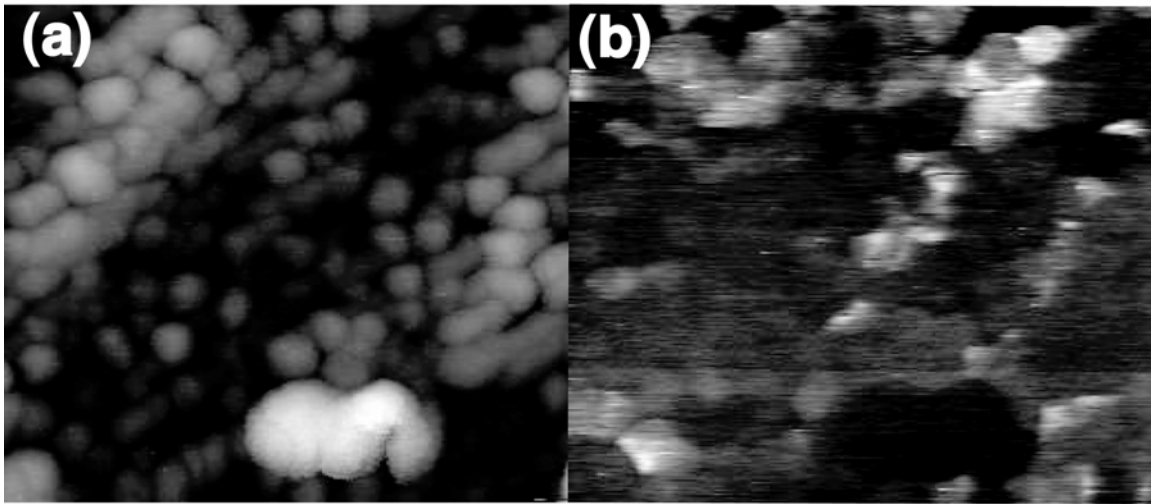

Fig. 1:   (a) STM topographic image of Au/TiOPc/GaAs heterostructure, recorded at T = 300 K, I_t = 5 nA, V_t = 1.4 V. (b) Corresponding BEEM image (recorded simultaneously with the STM image, color scale corresponds to 0 . . . 1 pA .

To investigate the transmission behavior of TiOPc, we systematically measured ballistic electron spectra on various positions of our sample.

To extract the barrier height, i.e. the onset voltage, from the measured data, we use a quadratic power law fit (see, e.g. [13]). The Bell-Kaiser model was not used because already the straightforward power law, despite of its simplicity, fits our data very well and is completely sufficient for our purposes. The barrier height values gained from the power fit are 1.24 eV and 1.18 eV for sample A and B. The histograms of the two samples are in Fig. 2 and 3. We measured an effective barrier height of Au/TiOPc/GaAs. It must be pointed out that at present, we can not decide if the measured barrier height is the barrier of the Au-TiOPc interface or the barrier of the TiOPc-GaAs interface or a combination of both. It is clear that is not the Schottky barrier height of Au/GaAs interface, because the onset we measured is significantly higher then 0.9 eV.
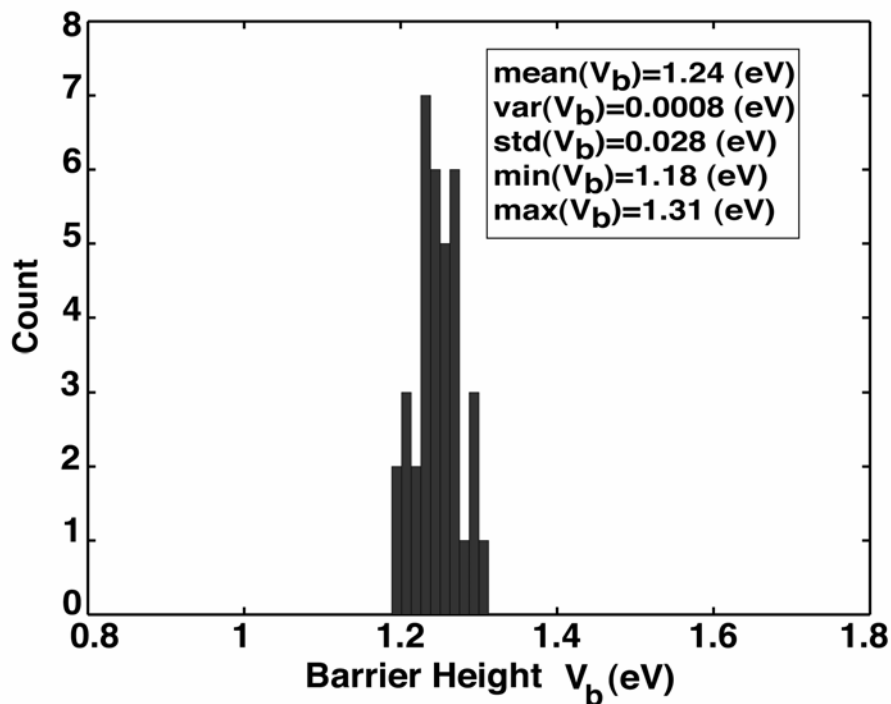
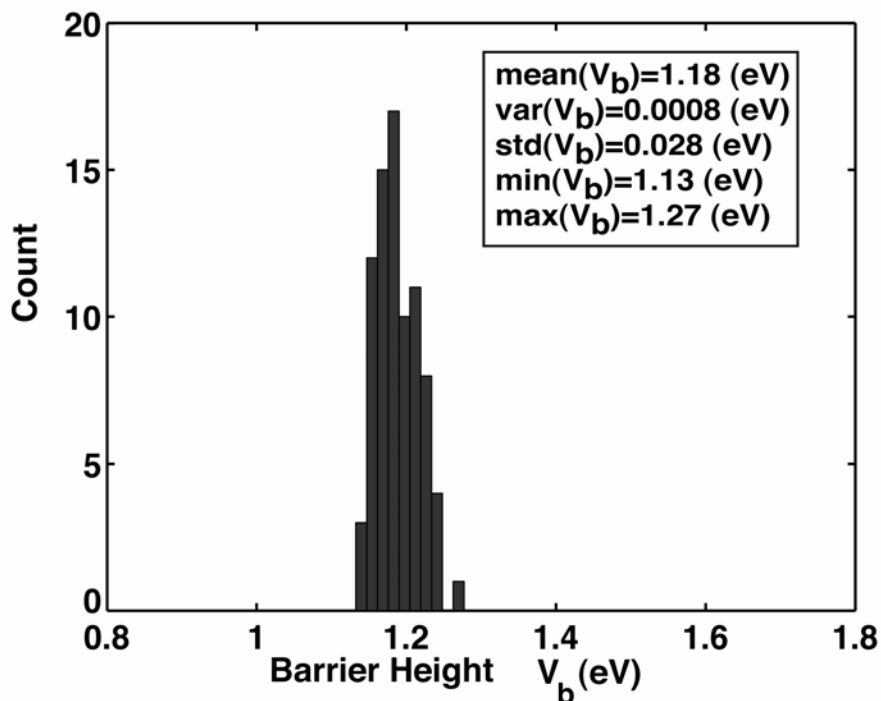Fig. 2: Histogram of the measured barrier height of Au/TiOPc/GaAs (sample A).

Fig. 3: Histogram of the measured barrier height of Au/TiOPc/GaAs (sample B).

The solid line in Fig. 4 shows averaged BEEM spectra (I_t = 5 nA, T = 300 K) and the dashed line is its first derivative taken of over 100 individual BEEM spectra. The spec-

tra are taken over a voltage-range of 0.8 to 2.3 V. Above the onset several features are visible, three steps at the points: 1.34, 1.52 and 1.61 V. The same behavior of metal-organic interfaces was also found in [16] – [18]. Besides these features there are two significant peaks at 1.7 and 1.85 V. Above 2.3 V the data were not reliable, because of the increased signal to noise ratio.
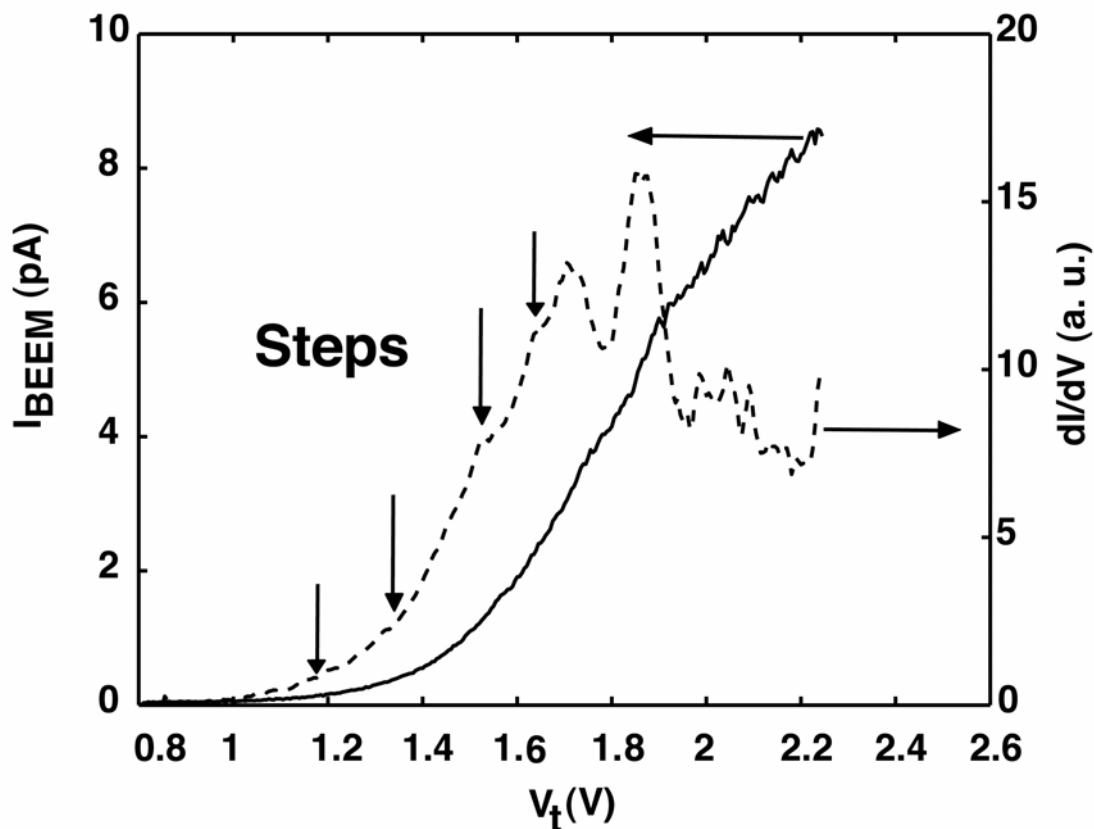

Fig. 4:   Averaged BEEM spectra (solid line) and its first derivative (dashed line) from Au/TiOPc/GaAs. Multiple features are clearly visible in the first derivative.

Conclusion

Due to the BEEM images, it can be concluded that the samples are very homogeneous, in comparison to wet chemically manufactured organic films. All features visible in the BEEM images of our samples correlate exclusively with the granular structure and the topographic features of the Au-film and cannot be correlated to the organic film underneath. Analyzing the BEEM spectra we find that the TiOPc increases the BEEM threshold voltage compared to reference Au/GaAs diodes, which was also found in [19], where a BEEM study on a Au/Molecule/n-GaAs diode was done. The barrier height measured on the Au-TiOPc-GaAs is $V_b \sim 1.2eV$, which is in good agreement with the data found in references [1]. The results indicate that TiOPc functions as a p-type semiconductor, which is plausible since the measurements were carried out in air [2]. In addition, the derivative of the BEEM spectra shows multiple features in the energy regime above the LUMO level [2]. Possible origins of these features are currently under investigation.

Acknowledgments

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