Ballistic Electron Transport Through Au/TiOPc/GaAs and Au/HBC/GaAs Diodes

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(Dated: March 8, 2010)

ABSTRACT
The understanding of charge transport through metal-organic and/or organic-semiconductor interfaces plays a significant role in the further development and improvement of molecular electronics. This paper presents a theoretical investigation of hot electron transport through organic films grown on GaAs. Ballistic electron transport through Au/TiOPc/GaAs and Au/HBC/GaAs is described by means of the Bell-Kaiser model. Good agreement between experimental results and the prediction of the heterostructure extension of the Bell-Kaiser model is reported showing that the Bell-Kaiser model extension can be used to describe the hot electron transport through metal-organic-semiconductor nanostructures.

1. INTRODUCTION

The in-depth understanding of the metal-organic and/or organic-semiconductor interfaces plays a significant role in the further development and improvement of organic and molecular electronics. Electron and hole transport is of great interest for the design of electronic devices such as light emitting diodes [1], organic transistors [2] and photovoltaic devices [3]. The continuing trend of device miniaturization requires a better understanding of the fundamental physics of the charge transport phenomenon on the nanometer scale.

One of the main challenges faced by the molecular electronics community consists in measuring and calculating charge transport through molecules. The ability to measure and predict conductivity of a single molecule is necessary and it requires the connection of a macroscopic current source and voltmeter to each end of a molecule. The connections should exhibit ohmic behavior with a low contact resistance, so that measured electrical characteristics can be unambiguously attributed to the molecule. Sufficient evidence exists to indicate that simply making physical contact between a metal and molecule is not enough to guarantee good electrical contact. The problem is compounded by the fact that the interfaces are buried under a thin film of metal. Therefore, the problem is one of contacts, how to make them, and how to characterize and predict their performance at length scales that are relevant for molecular electronics applications.

Ballistic electron microscopy/spectroscopy (BEEM/S) [4] has become a useful tool to study local properties of semiconductor interfaces and buried structures. BEEM is a three-terminal extension of conventional scanning tunneling microscopy (STM) [5], where ballistic electrons are injected from a STM tip into a semiconductor via a thin metal base layer evaporated onto the sample. The corresponding current, measured versus the tunneling bias using a back side collector contact, is called the BEEM spectrum. 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. In such BEEM images bright areas indicate enhanced electron transmission.

The organic semiconductors investigated in this work are titanylphthalocyanine (TiOPc) and hexa-*peri* hexabenzocoronene (HBC). The experimental BEEM results are prenset in Ref. [6, 7], those were prepared by molecular beam epitaxy (MBE). MBE grown GaAs samples were used as substrates, where low doped ($N_D \approx 1 \times 10^{16}$ cm^{-3}) GaAs layers ($d = 1\mu$m) were grown on an n^+-wafer. On these substrates, TiOPc films (nominal thickness of about 6 Monoloayers, corresponds to 1.9 nm) and HBC films (nominal thickness of about 4 Monoloayers, corresponds to 1.2 nm). As a final step, a 7 nm Au layer was evaporated prior to the BEEM measurements.

The organic semiconductor TiOPc is a phthalocyanine with the titanoxide (TiO) group protruding from its centre plane (for the molecular structure see Fig. 1). TiOPc has strong absorption and good photoconductivity in the near infrared (700–900 nm), which facilitates their use as photoconductors in diode laser-based printers [8-10]. TiOPc has become of special interest for many scientists all over the world due to its photogenerating properties when exposed to infrared light. This photogenerating activity in the near infrared makes it of use in photoreceptors designed for use in laser printers and digital copiers equipped with light emitting diode-arrays or laser diodes. HBC also has very interesting electric properties [11], structural formula shown in Fig. 2. HBC is often used as a relatively simple model compound, it can be found in the literature that HBC can be grown in large ordered domains [12]. Since HBC is used as a model compound there is a lot of investigations on the properties of HBC done as: ultraviolet photoelectron spectroscopy [13], self assembly at surfaces [14], electronic properties, ordered architectures of HBC at surfaces, nano-phase segregation and rectification in monolayers of functionalized HBC, observation of organic-organic heteroepitaxy, and charge transport in HBC.

In the present work, we demonstrate that the extension of the Bell-Kaiser model can also be used to describe the ballistic current through metal-organic-semiconductor heterostructures. The hot electron transport through the Au/titanylphthalocyanine (TiOPc)/GaAs and Au/hexa-*peri* hexabenzocoronene (HBC)/GaAs nanostructures is investigated by means of the heterostructure extension of the Bell-Kaiser. The calculated spectra are compared with the measurements reported in [6, 7]. The good agreement between experimental results and the prediction of the heterostructure extension of the Bell-Kaiser model is discussed. We stress that the Bell-Kaiser model extension can be used to describe the hot electron transport through metal-organic-semiconductor nanostructures with thin organic layers embedded. The transmission coefficients were calculated using the transfer matrix method.

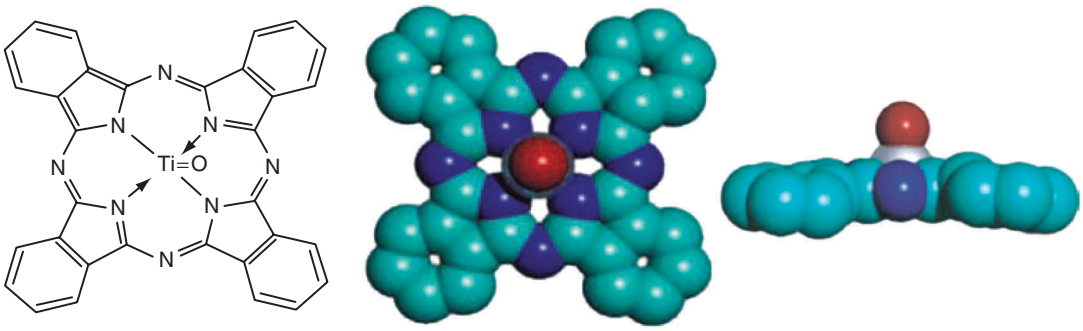

Figure 1. Molecular structure and space-filling model of titanylphthalocyanine ($C_{32}H_{16}N_8OTi$, TiOPc), top and side view.

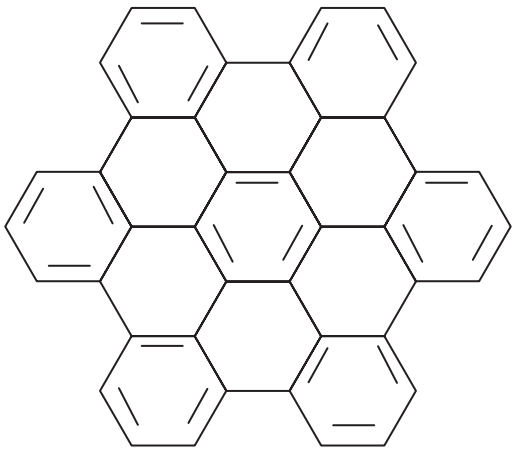

Figure 2. Structural formula of hexa-*peri* hexabenzocoronene ($C_{42}H_{18}$, HBC).

2. BEEM TRANSPORT THROUGH NANOSTRUCTURES

2.1. Conventional metal-semiconductor diodes

Measurements for Au/TiOPc/GaAs and Au/HBC/GaAs heterostructures, Schottky barrier height profiling and the temperature dependence of the Schottky barrier heights, are reported in [6, 7] respectively. In this article we focus on the transmission behavior of hot electrons through the Au/TiOPc/GaAs and Au/HBC/GaAs heterostructures.

Before we discuss the transport properties of Au/TiOPc/GaAs and Au/HBC/GaAs heterostructures we want to emphasize the transport through conventional metal-semiconductor diodes. For conventional metal-semiconductor diodes the so called Bell-Kaiser formalism [15] is used. Bell and Kaiser derived their formula by starting from the well-known formalism for tunneling between planar electrodes as an approximation. In this formalism, the STM tip and the base layer are assumed to be identical metals. Further, heterostructures incorporated into the collector, are not treated by the original Bell-Kaiser Model. We do not present the derivation of the Bell-Kaiser model in this short paper, a good description and derivation can be found in [16]. The BEEM spectra are described with the following formula, commonly known as the Bell-Kaiser-Formula:

$$I_c(V_t) = RI_{t0}\frac{\int_{E_z^{min}}^{\infty} dE_z T_{tb}(E_z)\int_0^{E_{xy}^{max}} dE_{xy}[f(E)-f(E+eV_t)]}{\int_0^{\infty} dE_z T_{tb}(E_z)\int_0^{\infty} dE_{xy}[f(E)-f(E+eV_t)]}, \tag{1}$$

I_c is the collector current, I_{t0} is the constant tunnel current at which the ballistic spectrum is measured, R is a measure of attenuation due to scattering in the Au layer, and T_{tb} is the transmission coefficient of the vacuum barrier which is calculated by a transfer matrix method [17]. The Schottky barrier height V_b appears in the coefficients $E_z^{min} = E_f - eV_t + eV_b$ and $E_{xy}^{max} = E_z - E_f + eV_t - eV_b$. The pre-factor R and V_b are fitting parameters. The Bell-Kaiser formula is well suited for fitting ballistic electron spectra on simple Schottky diodes in a voltage range of up to ≈ 200 meV above the onset. Eqn (1) describes our 7 nm Au/GaAs diode very well as one can see in Fig. 5 (a). In Fig. 5 (a) the dots are experimental values and the dashed line is a BEEM spectrum calculated with the conventional Bell-Kaiser model. The calculated BEEM spectrum yields a Schottky barrier height at the Au-GaAs interface of $V_b = 0.89$ eV, which is in very good agreement with the values from the literature [18, 19].

2.2. Metal-organic-semiconductor nanostructures

Fig. 3(a) shows a topographic STM image of the Au/TiOPc/GaAs nanostructure and in Fig. 3(b) the corresponding BEEM image is shown. 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 200×200 nm^2. 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.

To model the Au/TiOPc/GaAs and Au/HBC/GaAs nanostructures we use a extension of the above formula which is a modification of the original Bell-Kaiser model. We also use the conventional Bell-Kaiser model to show that one can fit also spectra of complex structures with eqn (1) but the yielded Schottky barrier heights are wrong. The modification of the original Bell-Kaiser model consists of an additional transmission coefficient T_{hs} to describe the properties of the heterostructure [20]:

$$I_c(V_t) = RI_{t0}\frac{\int_{E_z^{min}}^{\infty} dE_z T_{tb}(E_z)\int_0^{\infty} dE_{xy} T_{hs}(E_z, E_{xy})[f(E)-f(E+eV_t)]}{\int_0^{\infty} dE_z T_{tb}(E_z)\int_0^{\infty} dE_{xy}[f(E)-f(E+eV_t)]}. \tag{2}$$

In this expression E_{xy}^{max} no longer has to be declared explicitly, because the limit is now implicitly included via the dependence of T_{hs} on E_{xy}. To avoid quantum interferences between the vacuum barrier and the collector barrier, the transmission coefficients T_{tb} and T_{hs} are not combined into an overall

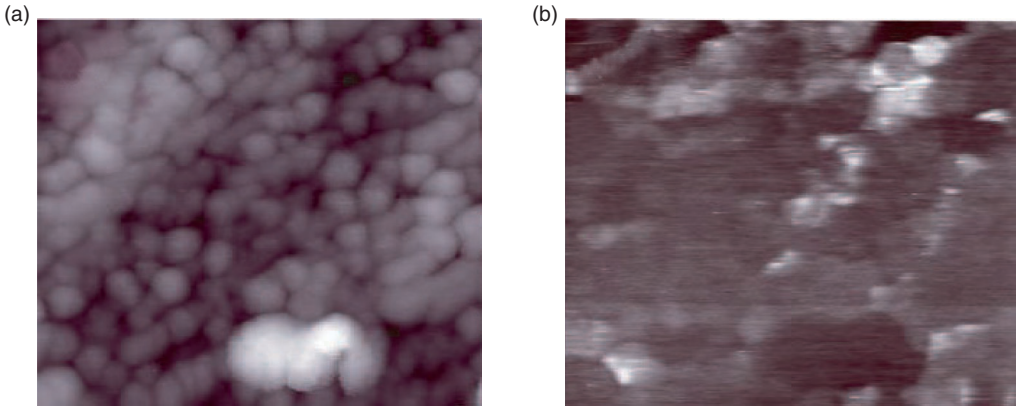

Figure 3. (a) STM topographic image of the Au/TiOPc/GaAs nanostructur. The image was recorded at $T = 300$ K, $I_t = 5$ nA, $V_t = 1.4$ V. The scansize is 200 nm × 200 nm. (b) Corresponding BEEM image recorded simultaneously with the STM image. The color scale corresponds to 0, …, 1 pA, brighter areas indicate an enhanced electron transmission.

transmission coefficient. To calculate transmission coefficients T_{hs} of the heterostructures we have used three piecewise constant potentials for Au-organic-GaAs respectively, with the height of the measured Schottky barrier and the width d of the organic layers, see in Fig. 4. The width d of the organic layers were 1.9 nm (corresponds to ≈ 6 Monolayers) for TiOPc and 1.2 nm (corresponds to ≈ 4 Monolayers) for HBC. The Fermilevel pinning at the organic-semiconductor interface, which is the difference between the Fermilevel of the complete nanostructure and the Γ-valenceband of GaAs, depicted as Γ in Fig. 4 are 1.1 and 1.2 eV for TiOPc/GaAs and HBC/GaAs interface respectively [6,7]. With the potential shown in Fig. 4 one can calculate the transmission coefficients T_{hs} using the transfer matrix method.

In Fig. 5 (b) and (c) the calculations for the Au/TiOPc/GaAs and Au/HBC/GaAs nanostructures are shown. The dots are the measured (meas.) values, the solid lines are the results of the extended Bell-Kaiser model (ext. BK) with additional transmission coefficients and the dashed lines are results of the conventional Bell-Kaiser model (con. BK). One can see in Fig. 5 (b) and (c) that the extended Bell-Kaiser model describes the experimental values very well. In table 1 are the calculated and

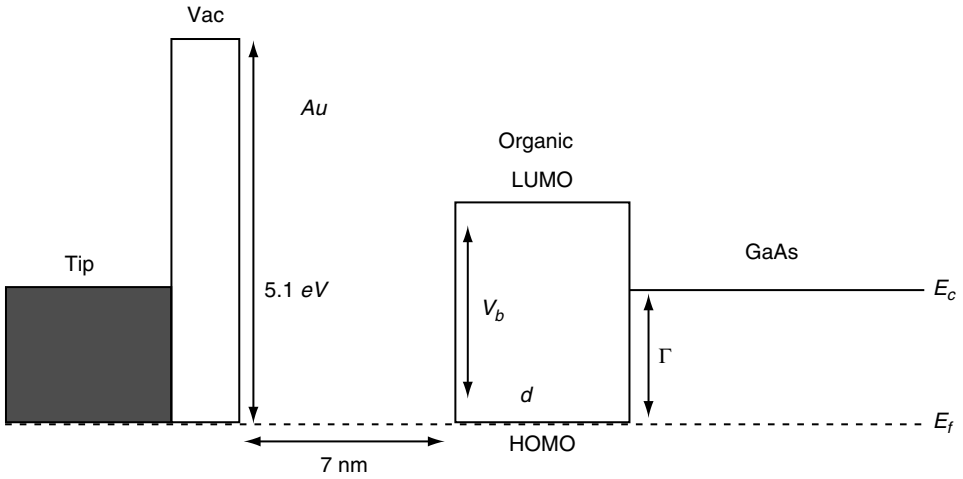

Figure 4. To calculate the transmission coefficient T_{hs} we have used three piecewise constant potentials for Au-organic-GaAs respectively, with the corresponding widths and heights, the height of the Au layer is zero because of the Fermi level alignment. HOMO and LUMO denotes highest occupied molecular orbital and lowest unoccupied molecular orbital respectively.

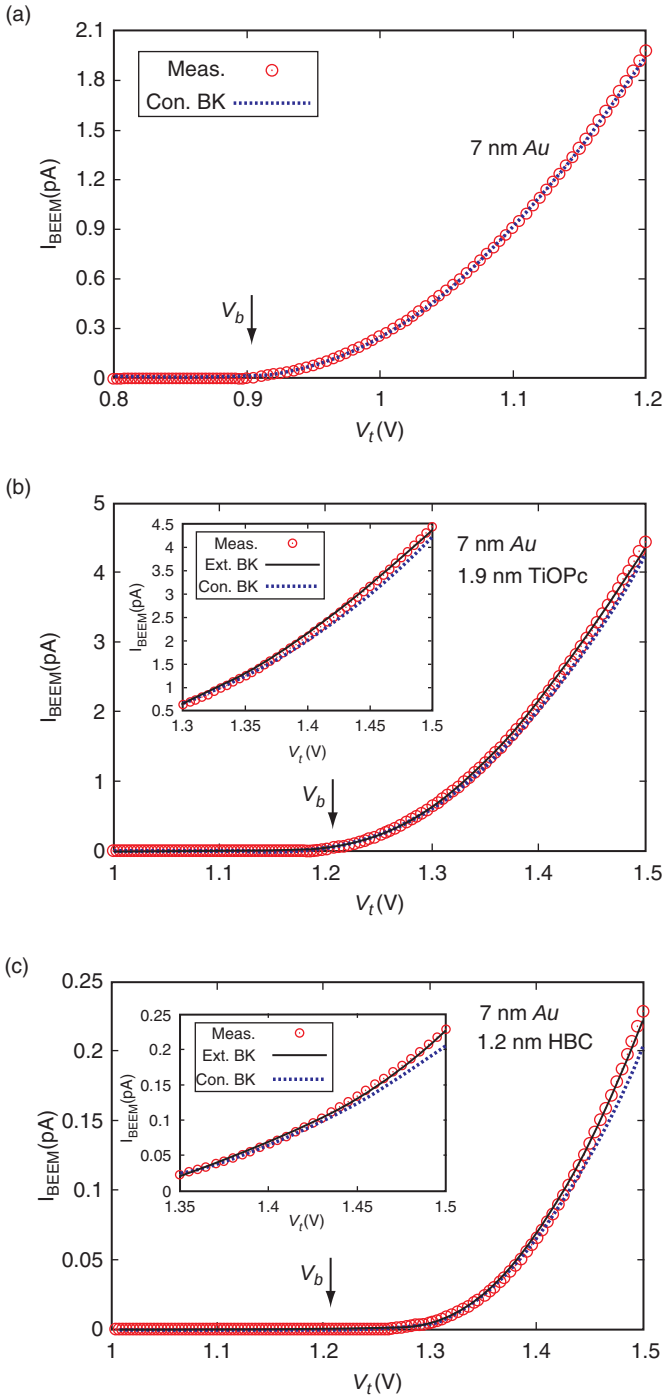

Figure 5. Averaged BEES spectra of Au/GaAs, Au/TiOPc/GaAs and Au/HBC/GaAs at 300 K. (a): Averaged BEES spectrum of 7 nm Au/GaAs, (b): 7 nm Au/1.9 nm TiOPc/GaAs and (c): 7 nm Au/1.2 nm HBC/GaAs. Solid lines are the calculated spectra using the extended Bell-Kaiser model, the dashed lines are calculated with the conventional Bell-Kaiser model, and the dots are the measured values. V_b denotes the Schottky barrier height.

Table 1. The calculated Schottky barrier heights of our nanostructures using the conventional Bell-Kaiser model and the extended Bell-Kaiser model. For comparison the experimental values are also shown.

	con. BK (eV)	**ext. BK (eV)**	**exp. (eV)**
Au/GaAs	0.89	–	0.89 Ref. [18, 19]
Au/TiOPc/GaAs	1.16	1.20	1.20 Ref. [6]
Au/HBC/GaAs	1.26	1.30	1.30 Ref. [7]

experimental Schottky barrier heights of our nanostructures. The calculation with the extended Bell-Kaiser model yields Schottky barrier heights of $V_b = 1.2$ and $V_b = 1.3$ eV for the Au-TiOPc and Au-HBC interface respectively, which is in excellent agreement with the measured values. The conventional Bell-Kaiser model yields wrong Schottky barrier heights for the nanostructures with organic layers embedded. Although the description of the organic layer with a simple constant rectangular potential is a crude simplification we obtain very good results.

The effect of temperature on the BEES spectra is illustrated in Fig. 6 (a) and (b) at 300 K 100 K and 10 K. The extended Bell-Kaiser model yields Schottky barrier heights of $V_b = 1.35$ and $V_b = 1.50$ eV

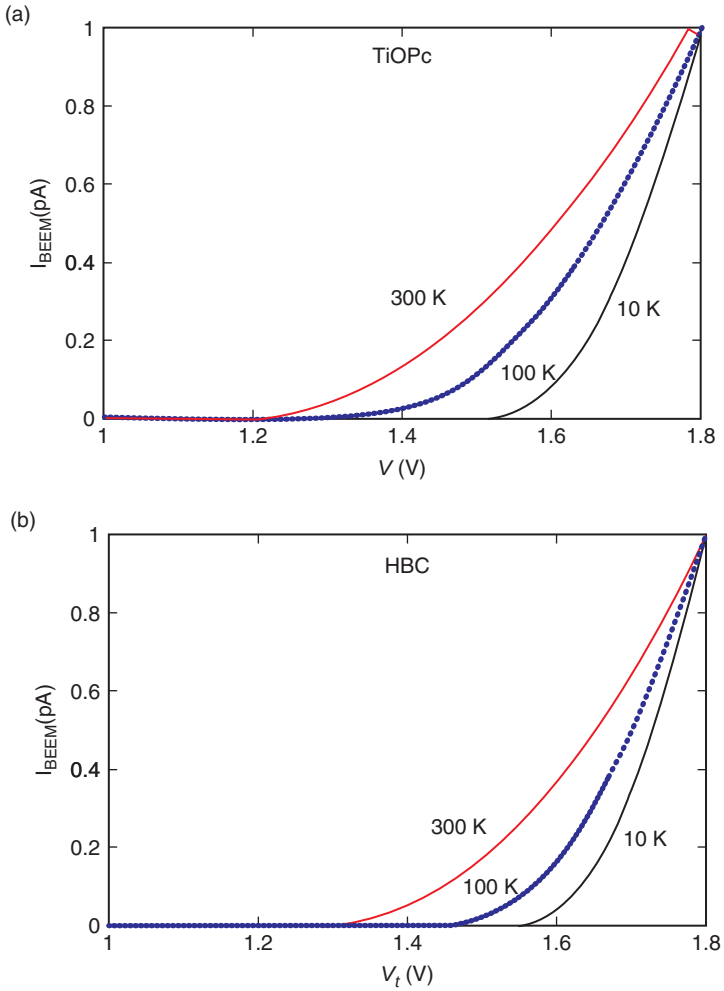

Figure 6. (a): Calculated BEES spectra using the extended Bell-Kaiser model of the Au/TiOPc/GaAs nanostructure. (b): Calculated BEES spectra using the extended Bell-Kaiser model of the Au/HBC/GaAs nanostructure.

for the Au-TiOPc and interface for 100 K and 10 K respectively. The calculated values for Au-HBC interface are $V_b = 1.45$ and $V_b = 1.55$ eV for 100 K and 10 K respectively. These values are in excellent agreement with the experimental values from Ref. [6] for the Au/TiOPc/GaAs and from Ref. [7] for the Au/HBC/GaAs nanostructure.

We think one can use the extended Bell-Kaiser model for BEEM spectra analysis of nanostructures including organic layers as long as the layers are thin enough, in our samples the organic layers were 1.9 nm and 1.2 nm for TiOPc and HBC. For such thin films one can justify the assumption of simple rectangular potentials. Additionally one has to be carefully when using the extended Bell-Kaiser model for energies ≈ 300 meV obove the onset V_b then the description becomes less accurate. This is because of two major reasons: first the influence of the GaAs *L* and *X* valleys was not included in the calculations, and second the the assumption of modeling the organic layers with simple rectangular potential barriers is not precise enough, like mentioned above.

3. CONCLUSION

We have investigated the electron transmission properties of Au/TiOPc/GaAs and Au/HBC/GaAs nanostructures with the conventional and heterostructure extension of the Bell-Kaiser model. For comparison also results for ordinary Au/GaAs diodes were shown. For the nanostructures with the organic layers embedded the conventional Bell-Kaiser model yields wrong Schottky barrier heights but for a conventional metal-semiconductor diode such as Au/GaAs it reproduces the experimental spectrum very well and yields the right value for the Schottky barrier height. We have shown that for the Au/TiOPc/GaAs and Au/HBC/GaAs nanostructures one can use the heterostructure extension of the Bell-Kaiser model for the hot electron transport. The model describes the experimental spectra very well for energies ≈ 300 meV above the onset V_b and gives the right values for the Schottky barrier height. We conclude that one can use the heterostructure extension of the Bell-Kaiser model for hot electron transport through nanostructures with thin organic layers embedded. The transmission coefficients were calculated using the transfer matrix method.

ACKNOWLEDGMENTS

We would like to thank the department of solid state electronics at the Vienna University of Technology (TU-Wien) for using the BEEM facilities.

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