Experimental investigation and simulation of hybrid organic/inorganic Schottky diodes

2003 J. Phys.: Condens. Matter 15 S2719

(http://iopscience.iop.org/0953-8984/15/38/010)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) S2719–S2728 PII: S0953-8984(03)65369-5

Experimental investigation and simulation of hybrid organic/inorganic Schottky diodes

A Bolognesi[1], A Di Carlo[1,3], P Lugli[1], T Kampen[2] and D R T Zahn[2]

[1] Dipartimento di Ingegneria Elettronica, Università di Roma 'Tor Vergata', Italy
[2] Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany

E-mail: dicarlo@ing.uniroma2.it

Received 26 June 2003
Published 12 September 2003
Online at stacks.iop.org/JPhysCM/15/S2719

Abstract

We have investigated electronic transport in hybrid organic/inorganic Schottky diodes. In order to derive from basic principles the transport properties of the organic semiconductors, we have use a two-dimensional drift-diffusion simulator which properly accounts for transport in both organic and inorganic layers. We have calculated the I–V characteristics of Ag/PTCDA/GaAs Schottky diodes as a function of PTCDA thickness and compared the results with experimental *in situ* measurements. The interplay between barrier height, PTCDA thickness, space-charge-limited current, and image charge is outlined.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The technological pressure generated by the ever-increasing demands of global telecommunication has led to the development of transmitters and receivers based on devices operating at very high frequency. Schottky diodes are often used for mixing applications in telecommunication systems, radio astronomy, radar technology, and plasma diagnostics [1]. However, for any low-cost mass produced device in telecommunication, satellite receivers, or automobile distance radar, the disadvantage lies in the relatively high bias voltage necessary in GaAs Schottky diodes, leading to high power consumption or low sensitivity combined with high requirements concerning the stability and noise of the voltage sources.

The electronic properties of a metal–semiconductor or Schottky contact are characterized by its barrier height. The barrier height is the difference between the edge of the respective majority-carrier band of the semiconductor and the Fermi level at the interface. The barrier heights of ideal, i.e. intimate, abrupt, homogeneous, and defect-free, Schottky contacts are determined by the continuum of metal-induced gap states (MIGS) [2]. Deviations from what

[3] Author to whom any correspondence should be addressed.

is predicted by the MIGS model may be attributed to secondary factors such as structure-related interface dipoles, interface structure, and interface defects, to name a few examples.

A reduction of the barrier height would significantly improve the device performance through lowering the power consumption. Several mechanisms may be used to tune the barrier heights of Schottky contacts. In Pb/Si(111) contacts, hydrogen has been employed to decrease and increase the barrier heights of Pb contacts on n-type and p-type Si(111), respectively. The results are explained by an additional hydrogen-induced charge of positive sign on the semiconductor side of the interface [3]. Instead of hydrogen, Vilan *et al* [4] used monolayers of small molecules to modify Au/n-GaAs diodes. Using a series of functional molecules whose dipole moment is varied systematically, the effective barrier height is tuned using the molecular dipole moment.

Instead of using monolayers of atoms or molecules, the barrier height may be tuned by using thin films of organic semiconductors with nanometre thickness. Organic semiconductors have seen a considerable development in recent years, mainly pushed by the realization of LEDs, displays, and organic thin-film transistors (TFTs). However, the low mobility of organic semiconductors precludes the complete replacement of compound inorganic materials especially for high-frequency applications. On the other hand, organic semiconductors can be used in hybrid organic/inorganic devices to tailor properties and performances of conventional devices.

The inclusion of well-defined molecular layers in inorganic Schottky diodes introduces a new degree of freedom in the control of fundamental device parameters. By means of the choice of the organic molecule and the interlayer thickness, the device can be designed to exhibit the desired properties. Depending on interlayer thickness, a variation from a pure semiconductor/metal junction to a pure inorganic/organic heterostructure is achieved, avoiding the complexity of inorganic semiconductor epitaxy. In principle, the introduction of interlayers consisting of conventional inorganic semiconductor materials is also feasible. However, the choice is strongly restricted by the necessary lattice match between GaAs and the interlayer material, resulting in expensive fabrication.

Forrest *et al* [5] have used PTCDA and N,N'-dimethyl-3,4,9,10-perylenetetracarboxylic diimide (DiMe-PTCDI) to modify metal/GaAs Schottky contacts. Their I–V characteristics can be understood using the thermionic emission space-charge-limited (SCL) transport model [6]. From their *ex situ* I–V measurements, they determined barrier heights which are, in most cases, larger than what can be obtained from metal-on-GaAs contacts.

An important property of organic semiconductors such as PTCDA is that the minimum energy for the formation of a separated free electron and hole pair, i.e. the transport gap $E_{\mathrm{trans}} = E_{\mathrm{LUMO,trans}} - E_{\mathrm{HOMO,trans}}$, is found to be considerably larger than the optical one involving exciton formation. The transport gap can be determined from the energy separation of the centre of mass of the HOMO and LUMO levels recorded by photoemission and inverse photoemission spectroscopy, respectively, and subtracting from this value the vibrational contribution and the difference between the bulk and surface polarization [7].

In this work, PTCDA was used as an interlayer for the modification of Ag/n-GaAs(100) Schottky contacts. The behaviour of organic/inorganic Schottky diodes is determined by comparing simulation results with experimental data. The electronic transport properties, or, in other words, the barrier heights, were investigated using *in situ* current–voltage (I–V) and capacitance–voltage (C–V) measurements as a function of thickness d_{PTCDA}.

Few attempts have been made to perform a physical simulation of the electronic devices. Alam *et al* [8] analysed the operation of an α-6T TFT using a two-dimensional drift-diffusion simulator. They showed that under certain conditions, one can describe the electrical characteristics of organic devices by using tools developed for inorganic semiconductors.

This is possible, because the basic transport parameters can be reinterpreted on the basis of the relevant physics of each material. In the following we will use a two-dimensional drift-diffusion simulator, able to describe organic/inorganic hybrid devices. Such an approach has already been used to describe the interplay between contact barrier height and mobility model in the output characteristics of organic TFTs [9].

2. Experimental details

Tellurium-doped n-GaAs(100) with a doping concentration of $N_D = 2 \times 10^{17}\,\mathrm{cm}^{-3}$ (Freiberger Compound Materials) served as a substrate. The substrate treatment used to prepare non-passivated GaAs(100) surfaces is the following. The substrates were first degreased in acetone, ethanol, and finally deionized water using an ultrasonic bath. To prepare non-passivated but nearly oxide-free surfaces, the substrate surfaces were etched in HCl for 30 s. The samples were then attached to a copper holder with an In–Ga alloy. After transfer into the ultrahigh-vacuum chamber, which has a base pressure of 3×10^{-8} Pa, the samples were annealed for 30 min up to a temperature of 300 °C. This leads to the formation of an InGaAs alloy on the back of the sample, resulting in a low series resistance of less than 20 Ω [10, 11]. During the last 5 min of the annealing, a hydrogen plasma treatment was carried out at a hydrogen pressure of 3×10^{-3} mbar. Atomic hydrogen reacts with arsenic and gallium oxides to form volatile compounds, thus removing residual oxides [12–14].

Organic molecular beam deposition was used to achieve the growth of the PTCDA layers at room temperature. Before use, the organic material was purified by vacuum sublimation. The deposition rates are between 0.3 and 0.8 nm min^{-1} and the thickness of the organic layer is controlled by a quartz crystal microbalance. One monolayer corresponds to 0.321 nm, which is the distance between the molecular planes in a PTCDA crystal, assuming flat-lying molecules [15]. Silver contacts with an area of 2.1×10^{-7} m^2 were evaporated through a shadow mask with a deposition rate of 7 nm min^{-1}. All I–V and C–V characteristics were recorded at room temperature (RT) *in situ* using a HP semiconductor test system.

3. Results

The I–V characteristics of Ag contacts as a function of d_{PTCDA} are shown in figure 1. The curve for the unmodified Ag contact may be described in terms of thermionic emission of carriers over a barrier, i.e. by (see, for example, [16])

$$I = FA^{**}T^2 \exp\left(\frac{-\phi_{\mathrm{B}n}}{k_{\mathrm{B}}T}\right) \exp\left(\frac{e_0 V_{\mathrm{a}}}{n k_{\mathrm{B}} T}\right)\left[1 - \exp\left(\frac{e_0 V_{\mathrm{a}}}{k_{\mathrm{B}} T}\right)\right]. \tag{1}$$

As usual, A^{**}, k_{B}, e_0, F, and T are the effective Richardson constant of n-GaAs, Boltzmann's constant, the elementary charge, the area of the contact, and the temperature, respectively, and I is the current. For applied voltages $V_{\mathrm{a}} > 3k_{\mathrm{B}}T/e_0 \approx 0.08$ eV at RT, the experimental I–V characteristics exhibit a linear behaviour in a semilogarithmic plot. Least-squares fits to these parts of the data give zero-bias barrier heights $\phi_{\mathrm{B}n}$ of 0.82 ± 0.01 and 0.59 ± 0.01 eV and ideality factors n of 1.1 ± 0.01 and 1.09 ± 0.01 for the Ag/GaAs(100) and Ag/S–GaAs(100) contacts, respectively. The voltage drop

$$V_R = RI \tag{2}$$

across a series resistance R with contributions from the GaAs bulk, its ohmic back-contacts, and external connections results in a deviation from straight lines for high forward biases.

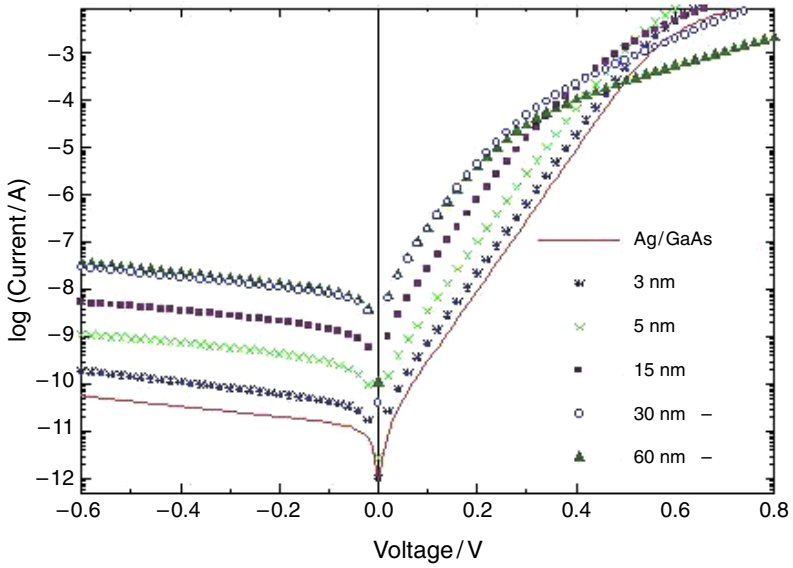

Figure 1. I–V-characteristics of Ag/PTCDA/GaAs(100) Schottky contacts as a function of d_{PTCDA} at RT. The contact area is 2.1×10^{-7} m^2.

With increasing d_{PTCDA} the current is increasing, indicating that the barrier height of the contact is effectively lowered. For reverse biases and forward biases below 0.2 V a behaviour typical for thermionic emission is observed. For a $d_{\mathrm{PTCDA}} > 5$ nm and applied voltages larger than 0.2 V the I–V characteristics are now influenced by the transport properties of the organic material. Transport through organic materials is governed by space-charge-limited currents (SCLC) which can be described by the Mott–Gurney law:

$$I = FA^{**}\mu \frac{V_{\mathrm{o}}^2}{d_{\mathrm{PTCDA}}^3}. \tag{3}$$

Here, d_{PTCDA}, V_{o}, and μ are the thickness of the organic layer, the voltage applied to the organic layer, and the mobility of the charge carriers in the organic layer, respectively.

For $d_{\mathrm{PTCDA}} < 30$ nm the flat-band barrier heights determined from the C–V characteristics of organic modified contacts have the same value as for the unmodified contacts. The C–V characteristics are completely determined by the capacitance of the space-charge region in the inorganic semiconductor, which does not change upon deposition of PTCDA. For $d_{\mathrm{PTCDA}} \geqslant 30$ nm, SCLC to dominates the I–V characteristics, and the capacitance of the organic layer starts to contribute significantly to the C–V characteristics.

4. Discussion

The barrier heights of the Ag/GaAs(100) contact can be analysed on the basis of the description of the hydrogen-modified Pb/Si(111) contacts already used. In both cases the Pauling electronegativity of the atom used for the modification ($\chi^{\mathrm{H}} = 2.2$) is larger than the electronegativities of the substrate atoms ($\chi^{\mathrm{Si}} = 1.9$, $\chi^{\mathrm{Ga}} = 1.81$, $\chi^{\mathrm{As}} = 2.18$). Therefore, an additional charge of positive sign is induced on the semiconductor side of the interface, resulting in an increase of the ionization energy of the clean surfaces and a reduction of the barrier heights at the metal–GaAs(100) interfaces [17, 18].

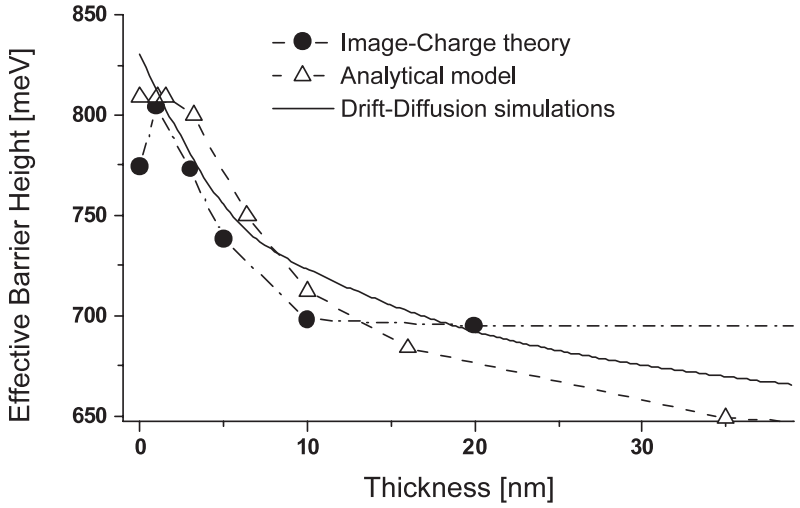

Figure 2. Effective barrier heights of Ag/PTCDA/GaAs(100) Schottky contacts as a function of d_{PTCDA} at RT. The three curves relate to: the barrier height obtained with the image-charge theory, equation (6) (closed circles); the barrier height extracted from experiments by using the analytical model of equation (4) (open triangles); the barrier height extracted from experiment by using the drift-diffusion simulations (solid curve).

For the determination of the barrier heights for the organic modified Ag/GaAs(100) Schottky contacts, the contributions of SCLC and series resistances to the charge transport have to be taken into account in addition to thermionic emission. The voltage drops over each contribution add up to the total applied voltage:

$$V = V_{\mathrm{a}} + V_{\mathrm{o}} + V_{\mathrm{r}}. \tag{4}$$

Inserting equations (1)–(3) in (4), the experimental I–V curves can be fitted, using $\phi_{\mathrm{B}n}$, n, μ, and R as fitting parameters. For the Ag/PTCDA/GaAs(100) contacts the effective barrier height decreases as a function of d_{PTCDA}. For $d_{\mathrm{PTCDA}} \geqslant 30$ nm, SCLC dominates the charge transport and the effective barrier height remains constant.

Figure 2 shows the resulting effective barrier heights for Ag/PTCDA/GaAs(100) contacts as a function of d_{PTCDA} together with the barrier heights calculated using the methods described in the next section. The change in barrier height as a function of d_{PTCDA} can be quantitatively explained using the energy level diagrams determined by photoemission spectroscopy shown in figure 3 [19]. The PTCDA does not change the electronic properties of the as-prepared GaAs substrate; i.e., the band bending is constant. For the plasma-treated substrate, the band bending in GaAs is determined as 0.8 ± 0.01 eV, which is the same as in Ag/GaAs(100) contacts. Starting with the lowest d_{PTCDA}, the effective barrier height is first constant and then decreases, indicating that $E_{\mathrm{LUMO,trans}}$ is approximately at the same energy or below the conduction band minimum (CBM) of the GaAs at the interface. With this result, the distance between $E_{\mathrm{LUMO,trans}}$ and the high-energy edge of the HOMO can be estimated to be 2.55–2.8 eV. A further increase in d_{PTCDA} results in a decrease in the effective barrier height.

5. Image charge

The decrease in effective barrier height observed for both types of substrate can be explained by a strong contribution for the low-dielectric-constant material PTCDA ($\varepsilon = 2$). If we consider

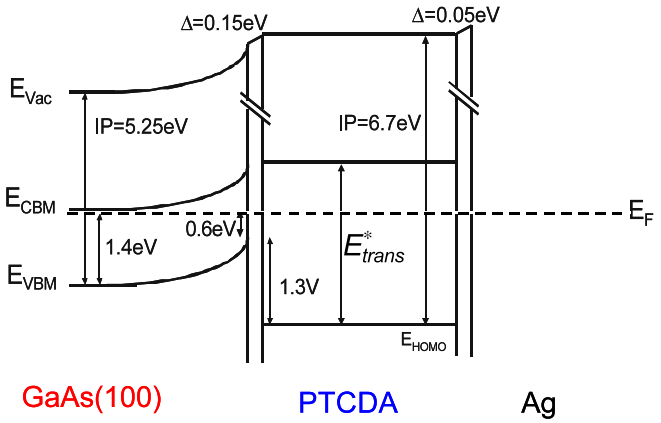

Figure 3. Band diagrams of Ag/PTCDA/GaAs(100) interfaces.

only the PTCDA/GaAs interface, the image force lowering can be calculated using (see [17])

$$\Delta\phi_{\mathrm{if}} = e_0\left[\frac{2e_0^2 N_{\mathrm{D}}(\phi_{\mathrm{B}n} - \xi - e_0 V_{\mathrm{a}} - k_{\mathrm{B}}T)}{(4\pi)^2(\varepsilon_{\mathrm{b}}\varepsilon_0)^3}\right]^{1/4}. \tag{5}$$

Here, $\xi = 20$ meV is the position of the Fermi level with respect to the CBM in the bulk, ε_{b} the dielectric constant of the inorganic semiconductor, and ε_0 the permittivity in vacuum. For Ag/GaAs(100) contacts, the image force lowering amounts to 50 meV. In a very simple approach, one may replace ε_{b} by the dielectric constant of PTCDA. This results in an image force lowering of about 200 meV which is in good agreement with the experimentally determined decrease in barrier height of 150 meV.

However, the correct description of the image force should consider the three-dielectric problem of the metal/PTCDA/GaAs system. In the metal/PTCDA/GaAs geometry (figure 4) the potential arises from a sum of infinite image charges [20] and is given by

$$\begin{aligned} V^{\mathrm{p}}(z) &= \frac{e^2}{2\varepsilon_{\mathrm{p}}L}\sum_{n=0}^{\infty}\frac{\xi^n}{n} + \frac{e^2}{2\varepsilon_{\mathrm{p}}}\frac{\varepsilon_{\mathrm{p}}-\varepsilon_{\mathrm{s}}}{\varepsilon_{\mathrm{p}}+\varepsilon_{\mathrm{s}}}\sum_{n=0}^{\infty}\frac{\xi^n}{|2z-(2n+1)L|} - \frac{e^2}{2\varepsilon_{\mathrm{p}}}\sum_{n=0}^{\infty}\frac{\xi^n}{|2z+(2n+1)L|} \\ V^{\mathrm{s}}(z) &= -\frac{e^2}{2\varepsilon_{\mathrm{s}}}\frac{\varepsilon_{\mathrm{p}}-\varepsilon_{\mathrm{s}}}{\varepsilon_{\mathrm{p}}+\varepsilon_{\mathrm{s}}}\frac{1}{|2z-L|} - \frac{2\varepsilon_{\mathrm{p}}e^2}{2(\varepsilon_{\mathrm{s}}+\varepsilon_{\mathrm{p}})^2}\sum_{n=0}^{\infty}\frac{\xi^n}{|2z+(2n+1)L|} \end{aligned} \tag{6}$$

where V^{p} is the image potential in the PTCDA and V^{s} is the image potential in the GaAs, and

$$\xi = -\frac{\varepsilon_{\mathrm{p}}-\varepsilon_{\mathrm{s}}}{\varepsilon_{\mathrm{p}}+\varepsilon_{\mathrm{s}}}$$

where ε_{p} and ε_{s} are the PTCDA and GaAs dielectric constants, respectively.

The conduction band edge profile of the Schottky diode for a constant electric field of 200 kV cm^{-1} (consistent with the typical field in the device), including the image potential, is shown in figure 5. The figure shows a clear overall reduction of the barrier height.

If we consider the maximum value of the conduction band edge as an estimate of the barrier height (without considering the singularity at the interfaces [21]), we find a barrier reduction of 110 meV. Moreover, for PTCDA thickness larger than 10 nm, the barrier reduction is negligible. In figure 2 we show the barrier height as a function of the PTCDA thickness as obtained with this method compared with the barrier heights extracted from experimental data via equation (4). We found an overall good agreement between the two curves. However, we should bear in mind that the effective value of the barrier high cannot be obtained considering

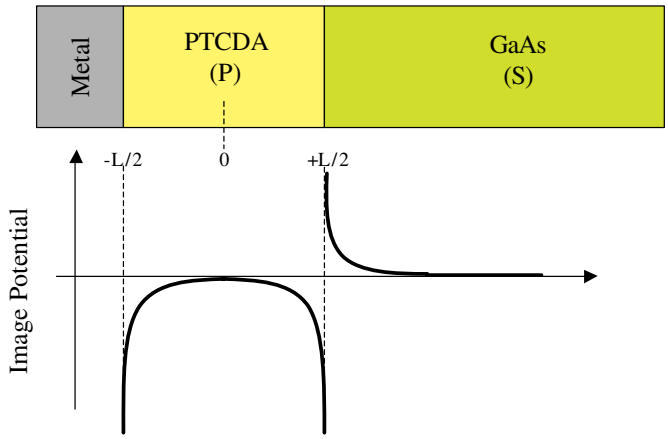

Figure 4. A schematic representation of the organic/inorganic Schottky diode and of the resulting image potential.

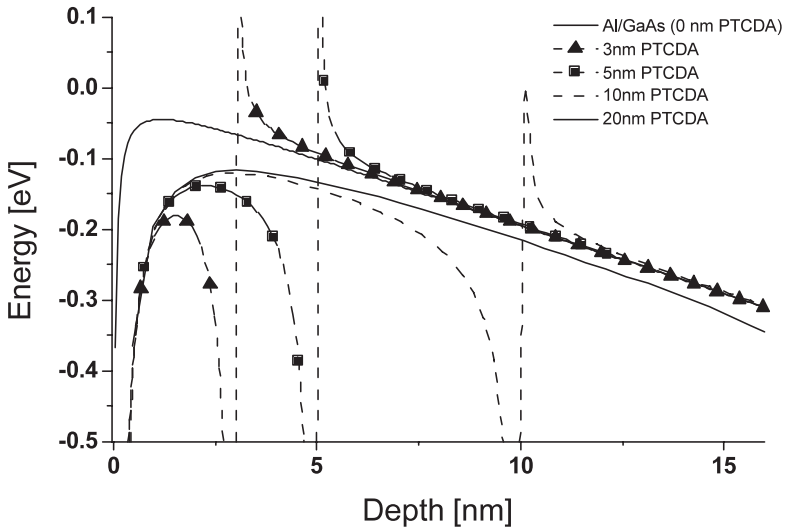

Figure 5. The conduction band edge for the PTCDA/GaAs Schottky diode as a function of the PTCDA thickness. The calculations were performed with a constant electric field of 200 kV cm^{-1}.

just the position of the band edge maximum, since tunnelling effects and their field dependences are quite important. Thus an accurate estimation of the effective barrier height should account also for tunnelling effects, which is beyond the scope of this communication.

5.1. Drift-diffusion simulations

We have used a drift-diffusion approach to compare the experimental curves with a physically based device simulation. The simulation tool is based on the solution of the equations

$$J_{\mathrm{n}} = -q\mu_{\mathrm{n}}\nabla V + qD_{\mathrm{n}}\nabla n$$
$$J_{\mathrm{p}} = -q\mu_{\mathrm{p}}\nabla V - qD_{\mathrm{p}}\nabla p$$
$$\nabla(\varepsilon_0\varepsilon_{\mathrm{r}}\nabla V) = -q(p - n + N_{\mathrm{D}}^{+} - N_{\mathrm{A}}^{-})$$

$$\frac{\partial n}{\partial t} = \frac{1}{q}\nabla J_{\mathrm{n}} + (G - R)$$
$$\frac{\partial p}{\partial t} = -\frac{1}{q}\nabla J_{\mathrm{p}} + (G - R)$$

where V is the electrostatic potential, n (p) the electron (hole) density, N_{D}^{+} (N_{A}^{-}) donor (acceptor) densities, J_{n} (J_{p}) the electron (hole) current density, μ the mobility, D the diffusion coefficient, G and R the generation rate and recombination rate, respectively. The transport in organic semiconductor can be obtained by a proper definition of the following quantities which are used in the DD simulation: (i) mobility; (ii) density of the states (DOS); (iii) equivalent doping; (iv) trap distribution; (v) band alignment between the organic semiconductor, inorganic semiconductors, and contact metals.

There are several models for mobility in organic semiconductors. In [8] the authors used a field- and temperature-dependent mobility based on the Holstein model [22]. In our calculation, based on Monte Carlo simulations [23], the field dependence of the mobility is given by

$$\mu(E) = \mu_0 \exp\left(\sqrt{\frac{E}{E_0}}\right)$$

where $\mu_0 = 10^{-3}$ cm^2 V^{-1} s^{-1} is the low-field mobility and $E_0 = 10^5$ V cm^{-1} is a critical field [24]. Further details about the simulation method can be found elsewhere [23]. DOS in organic materials are different to those of classical semiconductors. However, we can define the effective DOS as a single equivalent level on the edge of the bands [8]. Since, for the temperature that we consider, all the states are thermally accessible, we can put the effective DOS equal to the density of molecules.

The simulated device consists of a GaAs-based Schottky diode where between the metal and GaAs a thin layer of PTCDA is deposited. The GaAs has thickness 475 mm with a doping of 2×10^{17} cm^{-3}. For the PTCDA, in accordance with XPS measurements, we assume $E_{\mathrm{g}} = 2.55$ eV, an electronic affinity $\chi = 4.15$ eV, and a DOS $N = 2 \times 10^{22}$ cm^{-3}. The band alignment in metal–PTCDA–GaAs is shown in figure 3. In the simulations, a contact resistance of 300 Ω m has been considered for the GaAs back-contact.

The simulated output currents are reported in figure 6 for several thicknesses of the PTCDA layer. Here, the only fitting parameter is the barrier height. The values used for the barrier height are shown in figure 2. We observe that the barrier heights extracted from the drift diffusion are closer to the image-charge model of equation (6) than the ones extracted with the simple analytical model of equation (4).

The I–V characteristics of the Al/PTCDA/GaAs device present two different regimes: one for biases below 0.3 V, where the typical behaviour of a Schottky diode is obtained; and the other for biases greater than 0.3 V, where the transport is governed by SCL currents. For larger biases the current is limited by the contact resistance.

The overall agreement between the simulation and the experimental results is remarkably good and shows how the approach developed can treat organic and inorganic semiconductors on equal footing.

6. Conclusions

In the present communication we have fabricated, measured, and simulated organic–inorganic Schottky diodes. Parameters needed for the simulation have been obtained by XPS measurements and other techniques. The barrier heights of Ag contacts modified by PTCDA

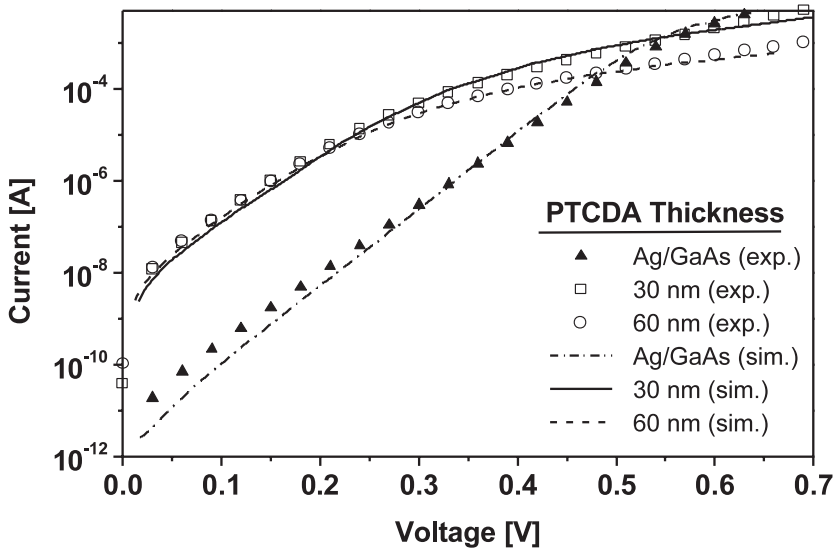

Figure 6. Comparison between experimental ('exp') and simulated ('sim') I–V curves for the PTCDA/GaAs Schottky diode for several values of the PTCDA thickness.

and the H-treated GaAs(100) substrates grown were investigated by means of *in situ* I–V and C–V measurements. Using the effects of the substrate treatment and organic layer thickness, the effective barrier height can be tuned between 0.65 and 0.81 eV. Here, the decrease in barrier height is explained by an increase in image force lowering, due to the PTCDA. In addition, the position of the LUMO transport level with respect to the high-energy edge of the HOMO can be estimated as 2.55–2.8 eV.

Acknowledgments

We are grateful to the Bundesministerium für Bildung und Forschung (BMBF, No 05 SE8OCA 7) and the EU-funded Human Potential Research Training Network 'DIODE' (contract No HPRN-CT-1999-00164) for financial support. We would also like to thank Freiberger Compound Materials for their support.

References

[1] Maas S A 1986 *Microwave Mixers* (Norwood, MA: Artech House Publishers)
[2] Heine V 1965 *Phys. Rev.* A **138** 1689
[3] Kampen T U and Mönch W 1995 *Surf. Sci.* **331–333** 490
[4] Vilan A, Shanzer A and Cahen D 2000 *Nature* **404** 166
[5] Forrest S R, Kaplan M L, Schmidt P H and Parsey J M Jr 1985 *J. Appl. Phys.* **58** 867
[6] Forrest S R, Kaplan M L and Schmidt P H 1984 *J. Appl. Phys.* **55** 1492
[7] Hill I G, Kahn A, Soos Z G and Pascal R A Jr 2000 *Chem. Phys. Lett.* **327** 181
[8] Alam M A, Dodabalapur A and Pinto M R 1997 *IEEE Trans. Electron Devices* **44** 1332
[9] Bolognesi A, DI Carlo A and Lugli P 2002 *Appl. Phys. Lett.* **81** 4646
[10] Lakhani A 1984 *J. Appl. Phys.* **58** 1888
[11] Ding A and Hsu C C 1996 *Appl. Phys.* A **62** 241
[12] Akatsu T, Plößl A, Stenzel H and Gösele U 1999 *J. Appl. Phys.* **86** 7146
[13] Elamrawi K A and Elsayed H E 1999 *J. Vac. Sci. Technol.* A **17** 823

[14] Yamada M and Die Y 1994 *Japan. J. Appl. Phys.* **33** L671
[15] Hirose Y, Chen W, Haskal E I, Forrest S R and Kahn A 1994 *J. Vac. Sci. Technol.* B **12** 2616
[16] Rhoderick E H and Williams R H 1988 *Metal–Semiconductor Contacts* 2nd edn (Oxford: Clarendon)
[17] Zahn D R T, Kampen T U, Hohenecker St and Braun W 2000 *Vacuum* **57** 139
[18] Hohenecker St, Kampen T U, Werninghaus T, Zahn D R T and Braun W 1999 *Appl. Surf. Sci.* **142** 28
[19] Park S, Kampen T U, Zahn D R T and Braun W 2003 *Appl. Phys. Lett.* submitted
[20] Kumagai M and Takagahara T 1989 *Phys. Rev.* B **40** 12359
[21] Serena P A, Soler J M and Garcia N 1986 *Phys. Rev.* B **34** 6767
[22] Holstein T 1959 *Ann. Phys.* **8** 343
[23] Bolognesi A, Di Carlo A, Lugli P and Conte G 2003 *Synth. Met.* **138** 95
[24] Bässler H 1993 *Phys. Status Solidi* b **175** 15
Hartenstein B *et al* 1995 *Chem. Phys.* **191** 321
Bässler H *et al* 1999 *Phys. Rev.* B **59** 7507
Bässler H 1999 *Semiconducting Polymers* ed G Hadziioannou and P van Hutten (Weinheim: Wiley)