

## Optimization of Current-Voltage Characteristics of Organic-on-Inorganic Heterostructure Diodes.

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Low barrier quasi-Schottky diodes for future microwave mixer applications are presented. The diodes are based on a heterojunction between an inorganic III-V semiconductor (GaAs, InP) and the aromatic compound PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) as a crystalline organic semiconductor. Measurements of the static I-V-characteristic with emphasis on the quadratic I-V behavior in forward direction and the use in microwave systems are discussed.

### 1. Introduction

High-performance microwave systems are becoming increasingly important for radar and communications. In these circuits, Schottky diodes are standard devices for detectors or mixers. In the radio frequency regime, Si-Schottky-diodes are available with forward voltages  $V(I = 10 \text{ mA}) > 150 \text{ mV}$ . However, GaAs-Schottky-diodes for higher frequencies up to 1 THz show typical forward voltages  $V > 500 \text{ mV}$  for comparable currents. Therefore, local oscillators with high power levels or dc biased circuits are required and increase the costs of the overall system.

These disadvantages can be overcome by a novel material combination of inorganic III-V and crystalline organic semiconductors. In addition to very promising intrinsic optical and electrical properties of the organic materials<sup>1)</sup>, they offer a number of further advantages. First of all, ultra-high vacuum (UHV) deposition and processing of organic crystalline layers are compatible with the conventional technology of inorganic semiconductors. Moreover, no lattice matching is required, and, due to substrate temperatures as low as  $T = 77 \text{ K}$ , the preparation of passive and active components on already processed devices becomes possible.

### 2. Sample preparation

From the enormous diversity of aromatic compounds the crystalline organic semiconductor PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) is chosen. The molecular structure and the monoclinic unit cell of UHV-deposited PTCDA are shown in Fig. 1. The molecules are ordered in stacks, and the molecular planes are parallel to the substrate surface with an interlayer distance of 0.321 nm. Due to this crystal geometry, electrical and optical properties show distinct anisotropies, e.g., the mobility of holes perpendicular to the substrate is  $\mu_{\perp} \approx 1 \text{ cm}^2/\text{Vs}$ , whereas the mobility parallel to the substrate is by a factor of  $10^2 \dots 10^3$  lower<sup>2)</sup>.

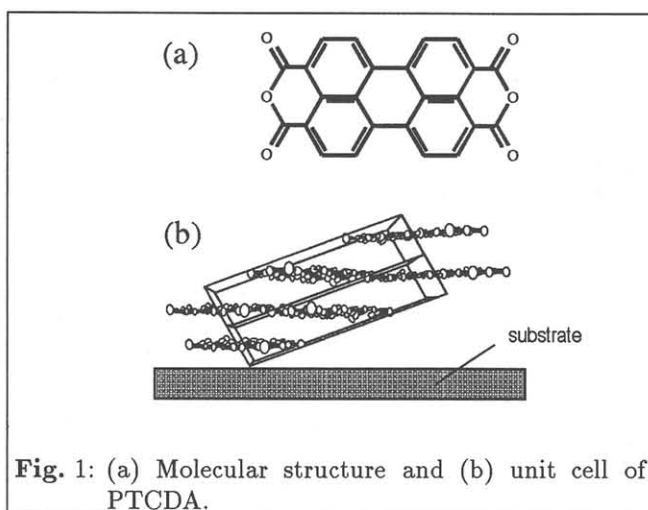


Fig. 1: (a) Molecular structure and (b) unit cell of PTCDA.

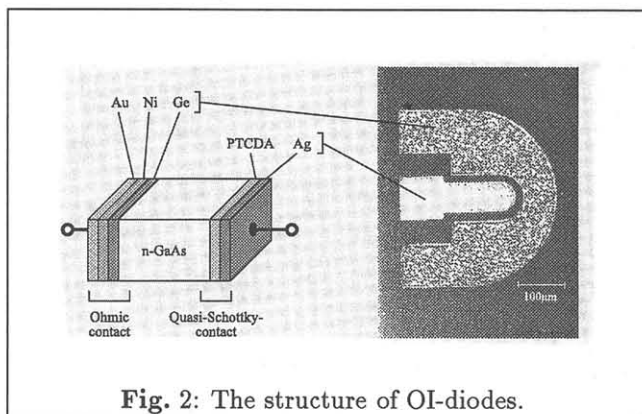


Fig. 2: The structure of OI-diodes.

As shown in Fig. 2, a planar structure is chosen for the investigation of organic-on-inorganic heterostructure (OI-) diodes. The lateral definition of the devices is achieved in two steps by conventional lift-off technique. In the first step, a Ge-Ni-Au multilayer metallization (20 nm/20 nm/160 nm) is deposited on the surface of the III-V wafer. For the formation of ohmic contacts, this process is followed by alloying Ge into the inorganic semiconductor substrate for 20 sec at a temperature of 350 °C for InP and 450 °C for GaAs. The second step consists of the fabrication of the center PTCDA finger with thicknesses from 0 nm to 20 nm, reinforced by a 160 nm Ag metallization. Since the GaAs substrates are only cleaned by dipping the samples into HF etch followed by rinsing with water, a thin oxide layer remains on the

substrate surface and affects the measurements. Thermal desorption under As stabilization may allow to overcome this problem. The organic layer is grown in an UHV organic molecular beam deposition system (OMBD), which is similar to conventional molecular beam epitaxy systems (MBE) for inorganic III-V semiconductors<sup>3</sup>). Prepurified PTCDA is sublimated from an effusion cell at 310°C and is deposited on substrates at temperatures of 77 K. Growth at a rate of about 0.1 nm/sec allow reproducible fabrication even of monolayer films.

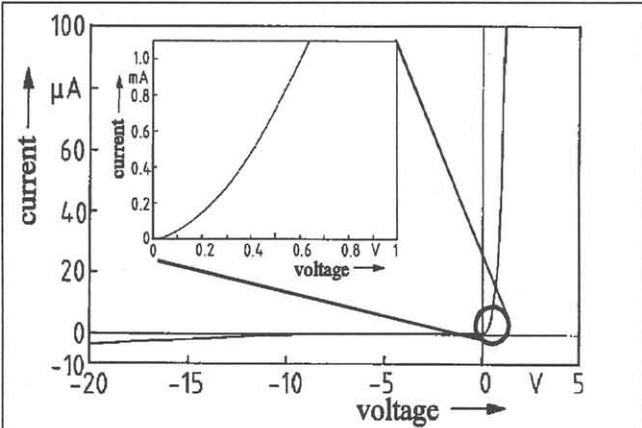


Fig. 3: I-V characteristic of a PTCDA-InP diode.

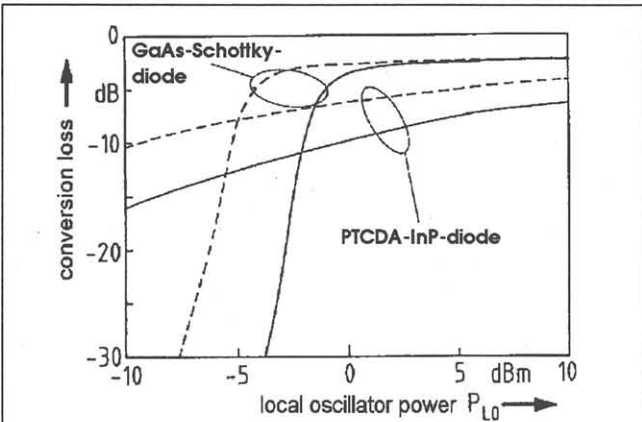


Fig. 4: Calculated conversion loss of a PTCDA-InP and a conventional GaAs-Schottky diode.

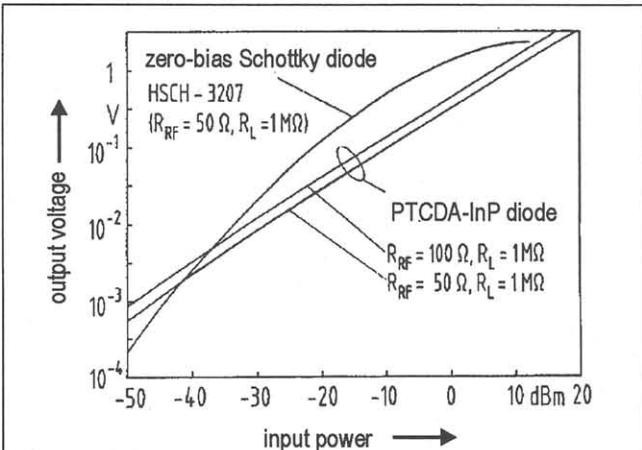


Fig. 5: Calculated output voltage of a PTCDA-InP and a zero-bias Schottky diode as microwave power detectors.

### 3. Experimental results

One of the first PTCDA/InP samples prepared exhibit a remarkable I-V characteristic shown in Fig. 3. The reverse breakdown voltage of the diode exceeds 20 V, whereas in forward direction a significant slope of the curve is observed near 0 V. This suggests a non-dc-biased operation in mixer applications with an essentially improved frequency conversion at low local oscillator power levels. Figure 4 shows the calculated conversion loss of this diode and of a conventional GaAs-Schottky diode in a single diode mixer circuit. Furthermore, due to the relatively low mobility and the low intrinsic hole concentration of  $n = 5 \cdot 10^{14} \text{ cm}^{-3}$ , the carrier transport in the PTCDA layer is space charge limited. In consequence, the forward I-V characteristic of the diode can rather be described by a square Mott-Gurney relation than by an exponential behavior<sup>4</sup>). Although this shape causes higher losses in mixer applications, an essentially improvement of linearity of analogue multipliers or power detectors can be obtained. Even in comparison with a zero-bias Schottky diode, which is optimized for these applications, OI diodes exhibit a distinctly more linear power detection (Fig. 5).

For device optimization, a detailed investigation of several influences on the static I-V characteristic is necessary. Fig. 6 shows a comparison of two OI diodes on GaAs substrates with different conduction types but equal doping concentration of  $N = 10^{18} \text{ cm}^{-3}$ . The OI interface exhibits in both cases rectifying behavior with a lower barrier height for n-GaAs. Because of this result and the expected better RF properties due to the higher electron mobility further experiments are performed only with n-type substrates. The influence of the doping concentration of the inorganic semiconductor is illustrated in Fig. 7. Forward voltages and reverse breakdown voltages depend strongly on the concentration and decrease for higher doping levels. In particular, even the sample with an extraordinary high doping concentration of  $n = 6 \cdot 10^{18} \text{ cm}^{-3}$  shows an asymmetric characteristic with a breakdown voltage of -1 V and a significant slope near 0 V in forward direction.

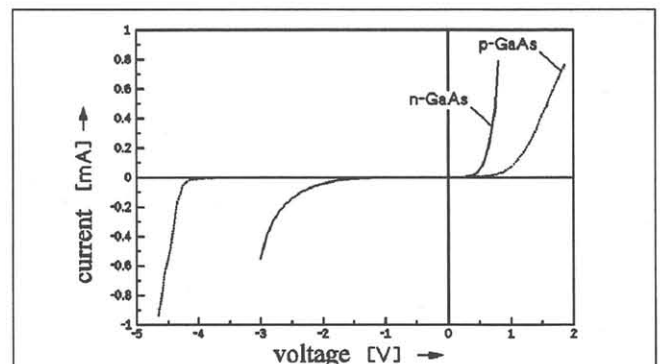


Fig. 6: I-V characteristics of OI diodes on n- and p-type GaAs ( $N = 10^{18} \text{ cm}^{-3}$ ).

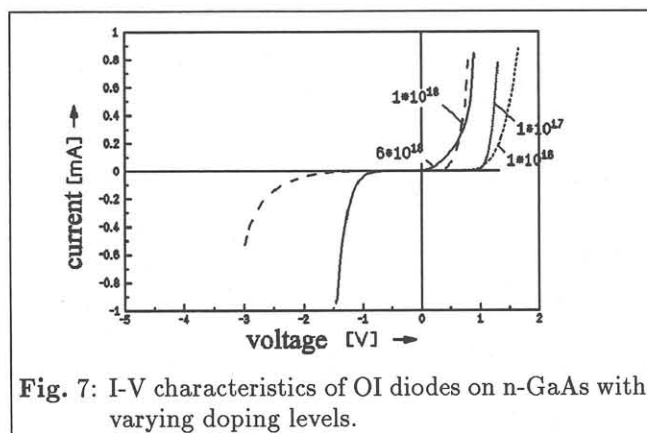


Fig. 7: I-V characteristics of OI diodes on n-GaAs with varying doping levels.

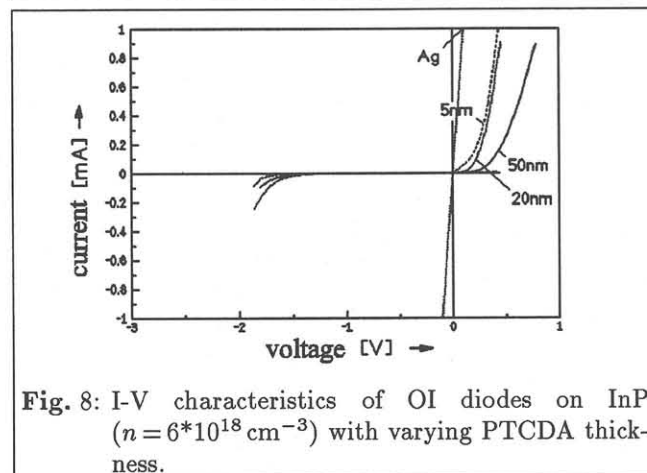


Fig. 8: I-V characteristics of OI diodes on InP ( $n = 6 \cdot 10^{18} \text{ cm}^{-3}$ ) with varying PTCDA thickness.

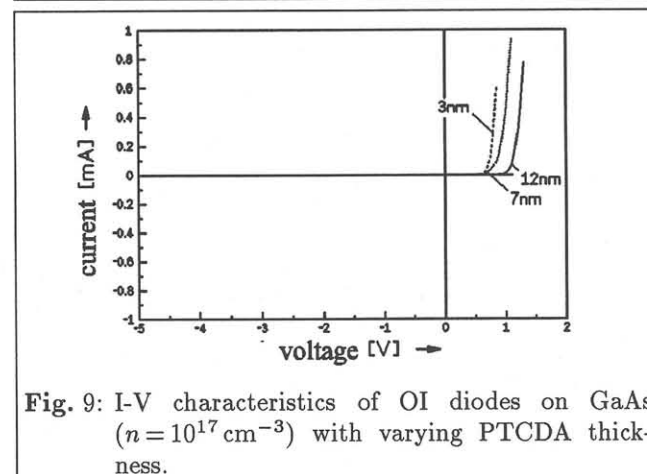


Fig. 9: I-V characteristics of OI diodes on GaAs ( $n = 10^{17} \text{ cm}^{-3}$ ) with varying PTCDA thickness.

Fig. 8 and 9 show the results obtained for devices based on GaAs and InP with an organic layer thickness varying from 0 nm to 50 nm. On both substrates the forward voltages can be reduced by decreasing the PTCDA layer thickness. In the limit, a pure Ag metallization without organic layer shows ohmic behavior. In consequence, the choice of a well defined PTCDA thickness is a simple way to control the barrier height of OI diodes. Furthermore,

the forward voltages and therefore the barrier heights on GaAs exceed the values on InP. This is mainly a result of the different doping concentration but, over and above that, it indicates a higher barrier of PTCDA or Ag on GaAs and might also be affected by the remaining oxide layer on the GaAs surface.

#### 4. Conclusion

We have presented a novel diode design with an additional thin crystalline organic layer sandwiched between an inorganic III-V semiconductor and the top metallization contact. The organic-inorganic heterojunction shows rectifying behavior, and, with regard to future microwave applications, remarkable I-V characteristics. On the one hand the forward voltages of these quasi-Schottky diodes can be reduced and easily controlled by the organic layer thickness. For this reason, non-dc-biased mixer applications with improved frequency conversion at low power levels become conceivable. On the other hand, a nearly square shape of the forward characteristic caused by space charge effects suggests very linear analogue multipliers or power detectors. Further investigations have to provide deeper insight into the influence of top metal and organic layer thickness onto the static behavior of these OI diodes. Dynamic characterization and optimization of the contact geometry with particular respect to mixer applications should follow and confirm the results obtained by DC measurements.

#### References

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