Extended Abstracts of the 1996 International Conference on Solid State Devices and Materials, Yokohama, 1996, pp. 586-588

Organic-on-InP Heterostructure Diodes for Microwave Applications

Peter URBACH, Dirk AMMERMANN and Wolfgang KOWALSKY

Institut für Hochfrequenztechnik, TU Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany.

Crystalline thin films of the aromatic compound PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) deposited on n-type InP substrates form quasi-Schottky diodes with very promising properties for nonlinear microwave circuits. The influences of doping concentration, film thickness, and contact metal on the static I-V-characteristics are discussed. In addition, measurements with network analyzers as well as C-V- and DeLoach-measurements allow to determine an equivalent circuit of the devices for the GHz regime.

1. Introduction

In the past decade, Schottky diodes for detectors and mixers in the THz regime have been developed. Whereas Si Schottky diodes for radio frequencies are available with forward voltages $V(I=10\,\mathrm{mA})>150\,\mathrm{mV}$, GaAs Schottky diodes for higher frequencies show typical forward voltages $V>500\,\mathrm{mV}$ for comparable currents. Therefore, high power levels or bias networks are necessary for practical applications and lead to increased overall costs.

On the other hand, investigation of electronic and photonic devices based on organic semiconductors have recieved more and more attention. It has recently been reported[1,2] that heterojunctions between PTCDA and conventional inorganic semiconductors show rectifying behavior. Moreover, ultra-high vacuum (UHV) deposition of thin organic films allows reproducible growth even of molecular monolayers. Further processing e. g. for a lateral definition of contacts is compatible with the conventional technology of inorganic semiconductors. Therefore, the possibilities for an optimization of organic-on-inorganic (OI) diodes with regard to special applications exist that overcome the disadvantages of conventional diodes by the novel material combination.

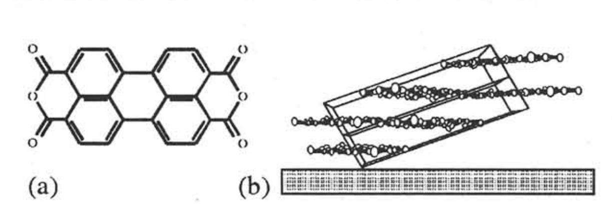

Fig. 1: (a) Molecular structure and (b) unit cell of PTCDA.

In Fig. 1 the molecular and crystalline structures of PTCDA are shown. The molecules are ordered parallel in stacks with an interlayer distance of 0.321 nm. This arrangement leads to distinct anisotropies of the electrical and optical properties. Due to the large overlap of π-electrons perpendicular to the molecular plane, a mobility up to $1\,\mathrm{cm^2/Vs}$ can be achieved in this direction, whereas the mobility parallel to the substrate is by a factor of $10^2 \ldots 10^3$ lower.

2. Sample preparation

The principle structure and the planar geometry of the fabricated samples are shown in Fig. 2. For the formation of ohmic contacts on the inorganic semiconductor, n-type InP substrates are cleaned and etched by $Br{:}CH_3OH$ to remove the oxide layer on the InP surface. Then, the Ge/Ni/Au metallization is deposited by e-beam-evaporation and laterally defined by conventional lithography with negative resist and lift-off. To achieve low series resistances, this process is followed by rapid alloying of Ge into the substrate at 330 °C. The formation of an oxide layer on the InP surface during this step is avoided by a reducing H_2/N_2 ambient.

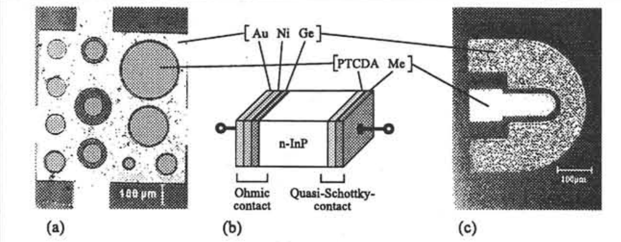

Fig. 2: The structure of OI-diodes for static measurements (a), for dynamic measurements (c), and the principle structure (b).

An optional lithography and SiO_2 sputtering process for a reduced PTCDA contact area can be inserted. Then, the organic semiconductor and the top metallization are deposited in an organic molecular beam deposition (OMBD) system[3]. For the growth of the organic layer, prepurified PTCDA is sublimated at 330 °C, which results in a growth rate of about 1 nm/min. The substrate temperature during growth is 77 K.

Since PTCDA is not completely resistant to organic solvents, the lateral definition of the contact can only be achieved by lift-off in the case of thin organic layers protected by a top metallization. It was also found that inhomogeneous metal films favor the penetration of the solvent into the PTCDA layer and the removal of the organic contact. For this reason, In leads to a very low number of sucessfully fabricated devices due to its rough surface, whereas Au or Ag show good results.

For critical samples, the organic contact can also be defined by a lithography process with positive resist combined with etching of the top metallization. Because of the anisotropy of the conductivity, the remaining PTCDA layer on the entire sample does not affect the device properties. For instance, an 8 s etch with 30 % HNO_3 was satisfactory for an Ag layer with 100 nm thickness.

3. Equivalent circuit

As reported elsewhere[2], the rectifying behavior of PTCDA/III-V heterojunctions is based on a depletion region in the inorganic semiconductor. The layer sequence of our devices then leads to an equivalent circuit shown in Fig. 3. The series resistance R_S describes the contact resistance of the ohmic Ge/Ni/Au-contact and a contribution due to the undepleted substrate material. The depletion region is represented by a voltage dependent junction capacitance $C_{oi}(V_{oi})$ and a junction resistance $R_{oi}(V_{oi})$. Contrary to conventional Schottky diodes, an additional capacitance C_o and a resistance $R_o(V_o)$ have to be inserted for the organic layer.

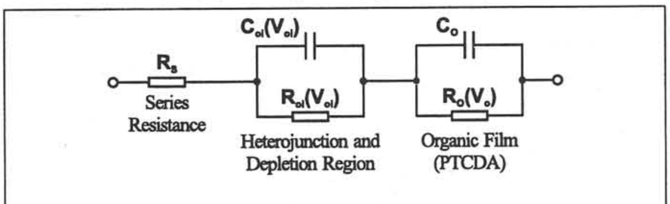

Fig. 3: The equivalent circuit of OI-diodes.

The ohmic contact area of the samples for dynamic measurements is approximately $1.3 \cdot 10^5\,\mu\mathrm{m}^2$. For instance, at a doping concentration of $n = 8 \cdot 10^{17}\,\mathrm{cm}^{-3}$, the resistance of the undepleted region can be estimated to be $< 100\,\mathrm{m}\Omega$, whereas contact resistances as low as $0.65\,\Omega$ are reachable. Therefore, the series resistance R_S should not exceed values of about $1\,\Omega$.

For mixer applications, additional series resistances should be avoided and, in consequence, thin PTCDA layers are required. In contact with high doped InP substrates, a large number of electrons migrates into the PTCDA film, and at thicknesses of about 5 nm and contact areas of $2 \cdot 10^4\,\mu$m it shows resistances in the mΩ regime. Therefore, the influence of the organic layer can be neglected for the calculation of the cutoff frequency, which is then given by $f_c = \frac{1}{2\pi R_S C_{oi}}$.

4. Results and discussion

The I-V-characteristics in forward direction of some selected samples with 10 nm PTCDA thickness are presented in Fig. 4. The forward voltages strongly depend both on the top metallization and the InP doping level. The lowest values of about $V(I = 100\,\mu\mathrm{A}) = 0.18\,\mathrm{V}$ were achieved with Ti and a doping concentration of $n = 6 \cdot 10^{18}\,\mathrm{cm}^{-3}$. At lower concentrations, tunneling currents through the depletion region are negligible, the series resistance increases and higher voltages are found. Moverover, the voltages also increase with Au as top metal, indicating a blocking barrier at the interface between Au and PTCDA.

In addition, the characteristics of the Au/PTCDA/InP diodes strongly depend on the history of operation and storage. The lowest forward voltages can be obtained immediately after the fabrication, and the device behavior remains nearly unchanged, if the current is limited to low values. When the currend exceeds a certain level, the next measurement shows an increased but stable forward voltage. After the devices were stored several hours at normal ambient, the forward voltage returns almost to its origin value. A similar and sometimes non-reversible change of the diode properties can also be found with other metals. To prove, whether this effect has a thermal cause, the samples were heated up to 140 °C and the I-V-characteristic was permanently monitored. In fact, the device behavior becomes instable at this temperature, but no significant change of the characteristic could be observed after cooling. Although this phenomenon has yet not been understood, it could be explained by charge filled traps at the interfaces causing blocking barriers of variable heights.

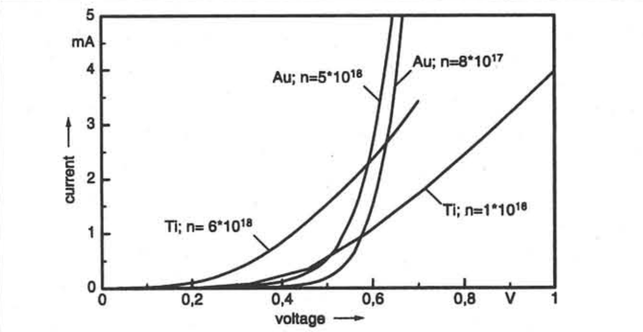

Fig. 4: I-V-characteristics of Ti and Au/PTCDA/InP diodes with different InP doping levels.

Due to the depletion region in the inorganic semiconductor, the reverse breakdown voltages of the diodes are nearly independent of the PTCDA thickness and the top metallization. Whereas values up to 20 V can be achieved on undoped InP substrates ($n < 1 \cdot 10^{16}\,\mathrm{cm}^{-3}$), the samples with a doping concentration of $n = 8 \cdot 10^{17}\,\mathrm{cm}^{-3}$ and $n = 6 \cdot 10^{18}\,\mathrm{cm}^{-3}$ exhibit only breakdown voltages of 3 V and 1.5 V, respectively. However, these values are sufficient for mixer applications. Furthermore, the values of the structures on undoped InP can be increased up to 40 V by a short HF dip immediately before loading them into the OMBD system. Therefore, surface contamination and thin oxide layers at the organic-inorganic as well as the PTCDA-top metal interface strongly affect the device properties and have to be removed for optimal device performance.

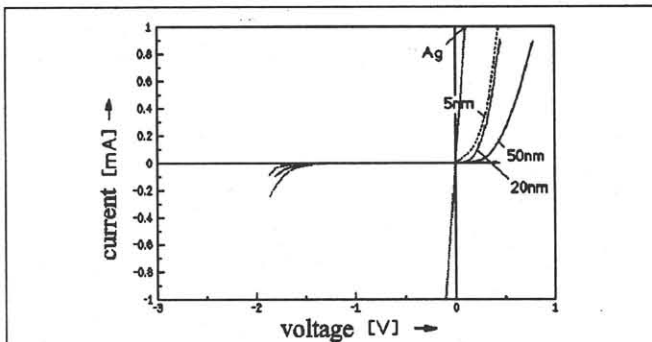

Fig. 5: I-V characteristics of PTCDA/InP diodes with varying PTCDA thickness ($n = 6 \cdot 10^{18}\,\mathrm{cm}^{-3}$).

The influence of the PTCDA thickness is illustrated in Fig. 5. These investigations were accomplished on $n = 6 \cdot 10^{18}\,\mathrm{cm}^{-3}$ doped InP substrates and with Ag top metallization. Obviously, 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. As a consequence, the choice of a well defined PTCDA thickness offers a simple way to control the barrier height of these diodes.

The results of samples with different top metallizations are summarized in table 1. For low forward voltages, metals with low work functions, e. g. Li, can also be used. Unfortunately, these materials are chemically very reactive and lead to a fast degradation of the devices. At first glance, the Li/PTCDA/InP samples showed very promising characteristics with low forward voltages, however, although the Li layer was passivated and reinforced by a Au metallization, instable behavior and increased forward voltages were observed after a few days. Furthermore, In as top metal also leads to low barrier devices, but, as mentioned above, offers technology problems. Finally, Ag is indeed very uncritical with regard to fabrication and degradation, but the samples are very sensitive to voltage peaks and high currents. Partial damage already leads to current filaments, which can be observed in the I-V-characteristics as ohmic parts. This effect attributes to the low voltages for Ag in table 1.

Contact metal	Forward voltage ($I = 100\,\mu A$)			Breakdown voltage		
	undop.	$8{\cdot}10^{17}$	$6{\cdot}10^{18}$	undop.	$8{\cdot}10^{17}$	$6{\cdot}10^{18}$
Ti	0.4 V	0.35 V	0.18 V	20 V	2 V	1.5 V
In	0.6 V	0.58 V	0.25 V	18 V	2.5 V	1.5 V
Li	>1 V	0.43 V	0.42 V	15 V	2.4 V	1.5 V
Ag	0.37 V	0.10 V	0.13 V	18 V	2.4 V	1.5 V
Au	>1 V	0.47 V	0.39 V	15 V	2 V	1 V

Table 1: Characteristics of Metal/PTCDA/InP diodes.

For dynamic characterization of the devices, DeLoach-measurements[4] in combination with C-V-measurements and an additional verification with network analyzers were carried out. The setup for DeLoach-measurements ist depicted in Fig. 6 and allows to determine the lead inductance, the junction capacitance, and the series resistance of the diode by measuring the transmision loss of the series resonance consisting of these three elements.

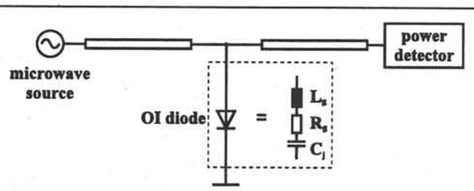

Fig. 6: Test setup for DeLoach measurements.

The results of these methods and the calculated cutoff frequencies are shown in table 2. For most samples, the values obtained from different measurements are consistent and the DeLoach data are used in the table. Due to instable operation and poor rectifying behavior, few samples led to different and unreliable results and were not included.

As expected, the listed values were only dependent on the substrate properties and quite independent of other parameters of the devices. Due to very thin depletion regions and contact areas of about $2 \cdot 10^4\,\mu m^2$, the high doped samples show comparable high junction capacitances up to 50 pF. On the other hand, series resistances below 1 Ω indeed indicate negligible influences of the organic layer and lead to cutoff frequencies in the GHz regime. Therefore, the applications of these devices could easily be extended to higher frequencies by inserting isolation layers for a reduced contact area and, in consequence, a reduced junction capacitance.

For undoped substrates higher series resistances up to 5 Ω were obtained, however, they are compensated by lower junction capacitances and lead again to cutoff frequencies of several GHz. Finally the Au/PTCDA/InP diode with an intermediate doping level still exhibits a very low series resistance yet an appreciable reduction of the capacitance is observed and therefore the highest cutoff frequency of 14.6 GHz is found. In combination with other top metals, this concentration provides also the best compromise between forward voltages and sufficient rectifying behavior.

Contact metal	Doping concentration	Series resistance	Junction capacitance	Cutoff frequency
Ti	undop.	5.1 Ω	9.8 pF	9.1 GHz
In	undop.	3.4 Ω	8.6 pF	5.4 GHz
In	$8 \cdot 10^{17}\,cm^{-3}$	0.8 Ω	46.9 pF	4.2 GHz
In	$6 \cdot 10^{18}\,cm^{-3}$	0.6 Ω	49.1 pF	5.4 GHz
Li	undop.	2.1 Ω	6.1 pF	11.4 GHz
Li	$8 \cdot 10^{17}\,cm^{-3}$	1.1 Ω	15.7 pF	8.9 GHz
Li	$6 \cdot 10^{18}\,cm^{-3}$	0.5 Ω	52.8 pF	6.0 GHz
Ag	undop.	2.7 Ω	7.4 pF	8.0 GHz
Ag	$8 \cdot 10^{17}\,cm^{-3}$	0.4 Ω	42.6 pF	9.3 GHz
Ag	$6 \cdot 10^{18}\,cm^{-3}$	0.3 Ω	52.5 pF	9.9 GHz
Au	undop.	3.0 Ω	8.1 pF	6.5 GHz
Au	$8 \cdot 10^{17}\,cm^{-3}$	0.3 Ω	36.2 pF	14.6 GHz
Au	$6 \cdot 10^{18}\,cm^{-3}$	1.0 Ω	44.4 pF	3.6 GHz

Table 2: RF parameters of Metal/PTCDA/InP diodes.

5. Conclusion

We have presented a novel diode design with an additional thin crystalline organic layer sandwiched between an inorganic InP substrate and different top metallization contacts. The organic-inorganic heterojuctions show rectifying behavior, and, with regard to microwave applications, remarkable I-V-characteristics and unexpected high cutoff frequencies. The forward voltages of these quasi-Schottky diodes can be reduced by suitable top metallizations, i. e. Ti, and is easily controlled by the organic layer thickness. For this reason, non-dc-biasedmixer applications with improved frequency conversion at low power levels become conceivable. The high frequency characterization of the devices has shown a large electron concentration in the PTCDA layer and, therefore, negligible contributions of the organic film to the series resistance and the cutoff frequency.

Further investigations have to provide deeper insight into the origin of additional blocking barriers at the interfaces both between PTCDA and the substrate and to the top metal. Furthermore, an optimization of the device structure for higher frequencies with smaller contact areas and a detailed investigation of frequency conversion should follow.

References

1) S.R. Forrest, M.L. Kaplan, and P.H. Schmidt, J. Appl. Phys. **55** (1984) 1492.

2) P. Urbach, C. Rompf, D. Ammermann, and W. Kowalsky, SSDM'95, Osaka, Japan (1995) 401.

3) C. Rompf, D. Ammermann, and W. Kowalsky, J. Mater. Sci. **11** (1995) 845.

4) B. DeLoach, IEEE MTT (1964) 15.