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Enhanced mixing characteristics of GaAs/3,4,9,10-perylenetetracarboxylic dianhydride Schottky diodes

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Abstract

The influences on the mixing properties of GaAs Schottky diodes containing an organic 3,4,9,10-perylenetetracarboxylic dianhydride layer were investigated. The frequency conversion ability of the devices was determined by considering the I–V characteristics and high frequency reflection parameters by using a mixing technique operated in the microwave range. The results show that an organic layer with 20 nm thickness enhances the diode conversion gain for mixing applications by 3 dB and lowers the device operating bias voltage by 0.1 V. This process is related to the specific properties of the organic semiconductor and resulting organic–inorganic interface.

1. Introduction

In the last few decades heterostructure diodes based on organic crystalline thin films deposited onto inorganic semiconductors have been a topic of increasing research interest [1–6]. Promising characteristics for microwave applications, due to the specific properties of the organic–inorganic interfaces, have been demonstrated [2]. The organic semiconductor 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) has been shown to have excellent properties for this propose [1]. On inorganic substrates (InP, GaAs) its molecules form well ordered crystals and due to the π-orbital overlapping a higher carrier mobility compared to other organic semiconductors is obtained. InP/PTCDA devices are superior to conventional GaAs diodes but the high cost of InP wafers could be a disadvantage [2]. Schottky diodes with an additional PTCDA layer based on GaAs have been investigated in the DC regime. Also the influence of the organic–inorganic interface quality on their properties was estimated recently [3–6]. But high frequency data and information on their capabilities as regards frequency conversion, receiving and processing signals have been generally lacking up to now.

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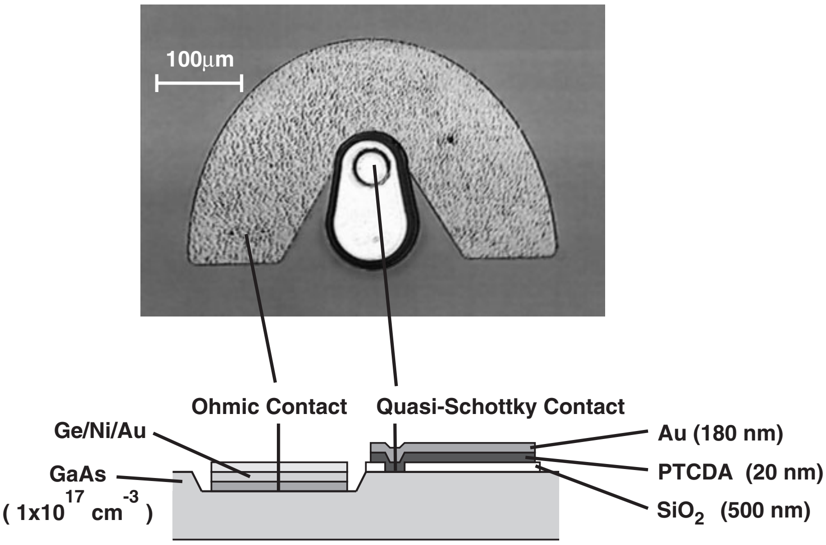

Figure 1. The device structure of organic-on-inorganic (OI) diodes.

This work considers the frequency characteristics of heterostructure GaAs/PTCDA diodes (figure 1) and shows how the organic–inorganic interface affects their signal mixing efficiency. Moreover, our device design, fabrication procedure and methods for characterization are close to those used in conventional semiconductor technology.

2. Basic parameters

Conversion of signals from high to low frequencies is one of the major applications of Schottky diodes. Device parameters such as the ideality factor n, barrier height Φ_{Bn} and junction resistance R_J can be extracted from current (I)–voltage (U) characteristics by plotting $\ln(I)$ and dU/dI versus U [7]. Since the mixing process takes place in the diode junction the junction capacitance C_J and serial resistance R_S are important parameters. Their values can be determined by considering the equivalent circuit of the device (figure 2) together with reflection measurements of the S-parameter S_{11} [2].

In general, the I–V behaviour of a real device can be represented in terms of a suitable polynomial series $I = \sum a_l U_l$. If a constant bias voltage U_B and two signals $U_{LO}\sin(2\pi f_{LO}t)$ and $U_{RF}\sin(2\pi f_{RF}t + \varphi_0)$ are applied, only for $l = 2$ is the resulting output U_{IF} linearly dependent on U_{LO}: $U_{IF} \sim U_{LO}U_{RF}\sin(2\pi(f_{LO} - f_{RF})t + \varphi_0)$, where f_{LO} (LO—local oscillator) and f_{RF} (RF—radio frequency) are the frequencies of the signals and φ_0 is the phase difference between them. For higher values of l non-linear terms are included which reduces U_{IF}. In this way the diode output in the case of two mixed signals is limited by the current flow and the shape of the I–V characteristics. The ideal mixing device should work in the ‘square law’ range, which is reached by setting an appropriate bias [8]. Space charge effects in the PTCDA and organic–inorganic interface broaden the range of the forward characteristics in which a square law can be assumed. This suggests improved linear output of the devices based on the combination of organic and inorganic semiconductors [1, 2].

The mixing efficiency is measured by the conversion gain (CG) which is defined as a ratio: $\mathrm{CG} = P_{IF}/P_{RF}$ where P_{RF} is the power of the RF signal and P_{IF} is the power of the output at

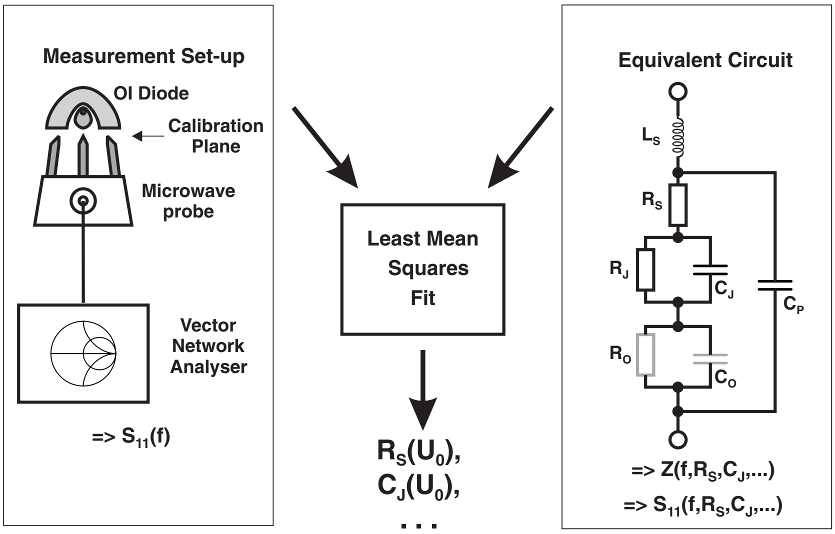

Figure 2. A schematic diagram of the microwave measurement method for determination of the equivalent circuit of OI diodes.

the intermediate frequency $f_{\mathrm{IF}} = f_{\mathrm{LO}} - f_{\mathrm{RF}}$. When P_{IF} and P_{RF} are measured in dBm,

$$\mathrm{CG\ (dB)} = P_{\mathrm{IF}}\ \mathrm{(dBm)} - P_{\mathrm{RF}}\ \mathrm{(dBm)}. \tag{1}$$

The plot of CG versus the power of the local oscillator P_{LO} characterizes the device conversion properties.

3. Device structure and preparation

The planar structure of the organic-on-inorganic (OI) diode (figure 1) is similar to that used in previous investigations [2]. The lateral geometry of the samples permits one to contact them with a ground–signal–ground configured microwave probe; i.e. it allows their characterization directly on the wafer. Four groups of diodes with different diameters (d) of the active area (0, 20, 40 and 80 μm) have been prepared.

As the first step of the production process, n-type GaAs substrates with doping concentration 1×10^{17} cm^{-3} were cleaned and etched for 10 min in HCl to remove the oxide layer on the surface. An 8 s dip in 1HBr:1CH$_3$COOH:1K$_2$Cr$_2$O$_7$(sat.):9H$_2$O offers good surface qualities. A Ge/Ni/Au (20 nm, 20 nm, 160 nm) metallization was used as the ohmic contact, structured by a conventional lift-off technique. Finally alloying was achieved by rapid thermal processing (60 s, 310 °C) in a nitrogen atmosphere. The active area of the diodes was determined by a 500 nm thick SiO$_2$ insulating layer with lithographically defined openings.

A second lithography process and evaporation of SiO$_2$ were performed to permit investigation of the microwave performance of the devices. In this manner, small active areas with low junction capacitances and sufficient contact space for testing and bonding can be obtained. Parasitic capacitances below 0.6 pF were achieved for the chosen geometry. A future benefit of the isolation pattern will be the enclosing of the PTCDA material and protection of it against additional oxidation when the sample is exposed to air.

Finally, the organic semiconductor and the top metallization (180 nm Ag layer) are deposited in an OMBD (organic molecular beam deposition) system [9] and laterally defined by a third lift-off process. The organic layer was deposited by sublimation of pre-purified PTCDA at 300 °C at a rate of 0.3 nm min^{-1} and a pressure of 5×10^{-8} mbar. Since the interface between the organic and inorganic semiconductors is responsible for the rectifying behaviour of the diodes, any additional barriers due to the surface oxidation of the GaAs would cause deterioration of their properties; e.g. the surface quality of the inorganic semiconductor has a fundamental influence on the device characteristics and stability. For this reason, the best results were obtained by adding a short HF dip (1%, 15 s) immediately before inserting the samples into the OMBD system. A reference set of devices without an organic layer was produced by the same technique.

4. Device characterization

To obtain the current–voltage characteristics we used conventional methods [10]. All measurements were performed in air.

The layer sequence of the diodes described leads to an equivalent circuit shown in figure 2. The series resistance R_S describes the ohmic Ge/Ni/Au contact and the resistance contribution of the undepleted substrate material. The depletion region is represented by the junction capacitance C_J and the junction resistance R_J. To represent the contact area defined by the insulating SiO_2 layer, a parasitic capacitance C_P should be added. Contrary to the case for conventional Schottky diodes, an additional capacitance C_O and resistance R_O have to be inserted for the organic layer. The value of R_O can be estimated by comparing the slopes of the I–V characteristics in the part where they are governed by the serial resistance for the samples with and without an organic layer. We find that C_O and R_O are negligible for diodes used in mixer applications. This is also valid for a lead inductance L_S when the devices are characterized directly on the wafer [2].

A method operating in the microwave regime was applied to obtain the parameters C_J and R_S (figure 2). By using a vector network analyser and calibration of the set-up with respect to the contacting plane of the diodes, the complex scattering parameter S_{11} can be measured as a function of frequency. The reflection can also be calculated from the device equivalent circuit. To obtain coincidence of the two curves, a least squares algorithm is applied and in this way C_J and R_S are determined [11].

The electrical scheme shown in figure 3 was used for investigation of the mixing capabilities of our samples. LO and RF are sources generating the signals with frequencies f_{LO} and f_{RF}. The narrow band pass yttrium–iron garnet (YIG) filter cuts out unwanted additional harmonics which would lead to additional losses. A microstrip filter network is used for separation of the high frequency parts from intermediate frequency ones and to supply the diodes with optimum bias. For adjustment of the output a double stub tuner and matching network are included in the circuit. All relevant parameters are tuned for each device individually.

5. Results and discussion

In figures 4(a) and (b) we show the current–voltage characteristics of the reference samples without an organic layer and samples with an additional 20 nm PTCDA layer respectively. The ideality factor of the organic–inorganic diodes is 1.60 ± 0.32 and higher than 1.24 ± 0.20 is obtained for the Ag/GaAs devices. This can be explained by an additional barrier added due to the PTCDA, as the I–V curves of the samples with PTCDA have higher onset voltages. Similar values are reported in [3] where the measurements have been carried out in air.

The values obtained for the barrier height (Φ_{Bn}) for the two types of device are similar and equal to 0.76 ± 0.04 V. This suggests that there are no general changes in the energy level

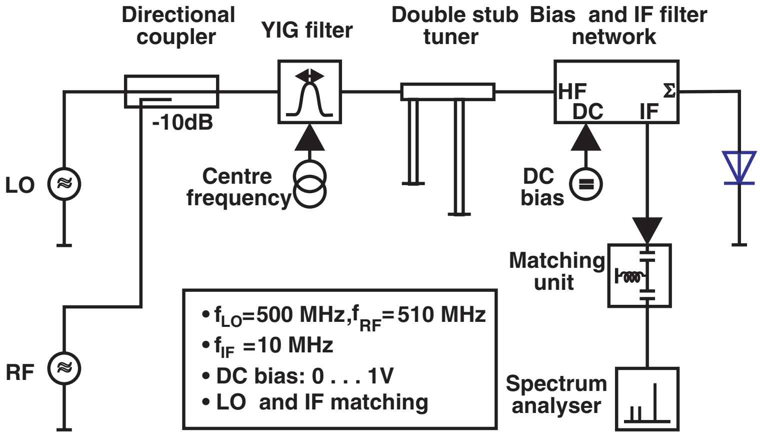

Figure 3. The electrical scheme for the measurement of the mixing characteristics of the diodes.

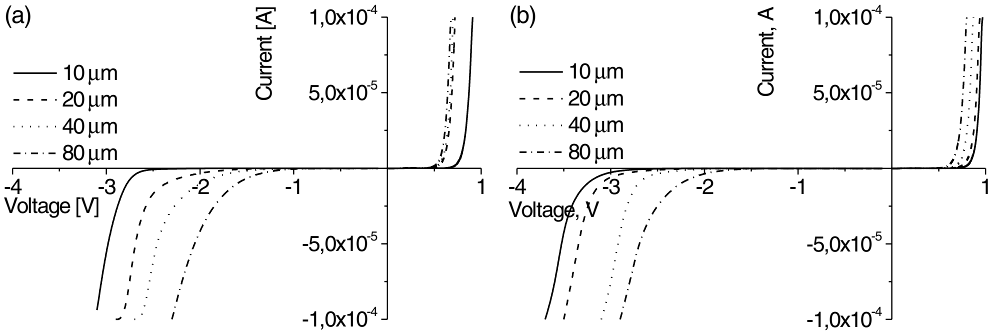

Figure 4. Current–voltage characteristics of reference samples without an organic layer (a) and a diode with a 20 nm PTCDA layer (b) for different active area diameters.

alignment of the GaAs and the metal contact due to deposition of PTCDA. However, a decrease of the barrier height with increasing thickness of the organic layer for samples measured in vacuum is reported [6]. The values of Φ_{Bn} are comparable with those obtained in [6] for Ag/PTCDA/GaAs samples and show that the processes at the organic–inorganic interface of the structure investigated are similar to those described elsewhere [4–6].

Reflection measurements were performed for the frequencies from 50 to 2000 MHz. The correlation with the S_{11} values obtained from the equivalent circuit contains a maximum uncertainty of 4%. For most of the measurements it is about 2%. The dependence of the serial resistance R_S on the device geometry is shown in figure 5(a). The values for the two types of device are comparable and they slightly decreased with increasing size of the contact area. With unchanging ohmic contact geometry, the serial resistance is affected by the size of the contact area, which can be explained by the increase in importance of edge effects as the diameters reduce.

As the frequency conversion takes place in the diode junction and considering the equivalent circuit (figure 2), the losses of the mixing signal are proportional to C_J. Thus the lowered C_J values obtained for samples with an organic layer (figure 5(b)) suggest an improvement of the mixing characteristics and CG. Changes in the device geometry cause an increase of the capacitance for both types. The ratios between the C_J values for diodes with

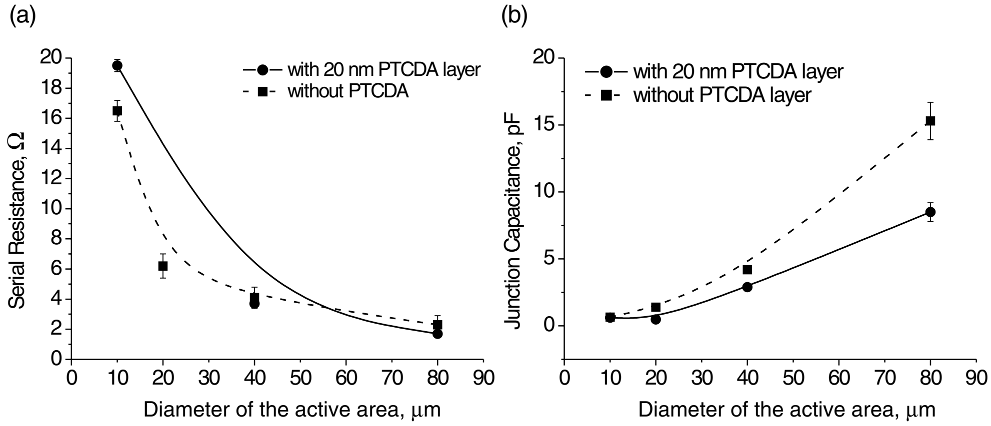

Figure 5. Comparison of the serial resistance (a) and the junction capacitance (b) of Ag/PTCDA/GaAs and Ag/GaAs diodes. The curves are intended as guides to the eye.

different values of d correspond to the ratios of the contact areas. However, the C_J values obtained do not fit with the simplified method proposed in [1]. Serial connection between the capacitance of the organic layer and C_J of the reference diode gives unrealistically low values for the resulting junction capacitance of the Ag/PTCDA/GaAs diode [6]. A possible explanation of the observed dependence is the existence of trapped charges in PTCDA crystal defects and additional capacitance of the organic–inorganic interface. This suggestion is also supported by the observation that the two devices with the smallest contacts have similar capacitances. As regards the organic layer, the difference in C_J increases with increasing active area.

The approximate cut-off frequencies of the devices described can be estimated from $1/(6.28 \times C_J R_S)$, where the capacitance and serial resistance are taken at 0 V bias. The values lie in the gigahertz range, can be larger than the corresponding ones for flat band conditions and are not useful for practical consideration [7].

The mixing capabilities of the organic–inorganic diodes were investigated directly by using the scheme shown in figure 3. The radio frequency power P_{RF} was set to a low value of -30 dBm and an optimum bias was applied to obtain a maximum IF signal output. A calibration against the losses in the matching circuits, directional coupler and YAG filter was performed. First, the available LO and RF powers at the port where the test diode was to be measured (labelled ‘sum’ and placed at the end of the circuit) were measured. In this case a proper termination of the IF port of the ‘bias and IF filter network’ was ensured. The measured CG versus P_{LO} for the device with a PTCDA layer is presented in figure 6(a). The diodes with $d = 80$ and 10 μm show the lowest CG values. This is caused by the largest C_J being for the sample with 80 μm diameter of the active area and the larger current flow through both when the optimum bias is applied. The devices with 40 μm diameter of the contact area seem to have an optimal geometry for mixing signals with the frequencies used.

The results for the reference devices show similar behaviour and the samples with $d = 40$ μm also show the highest CG.

A comparison between Ag/PTCDA/GaAs and devices without an organic layer is shown in figure 6(b). The samples with optimal geometry from both groups were chosen. The results clarified that the 20 nm thick PTCDA layer enhances the device mixing properties by lowering the junction capacitance and restricting the current flow through the diode. Moreover, the

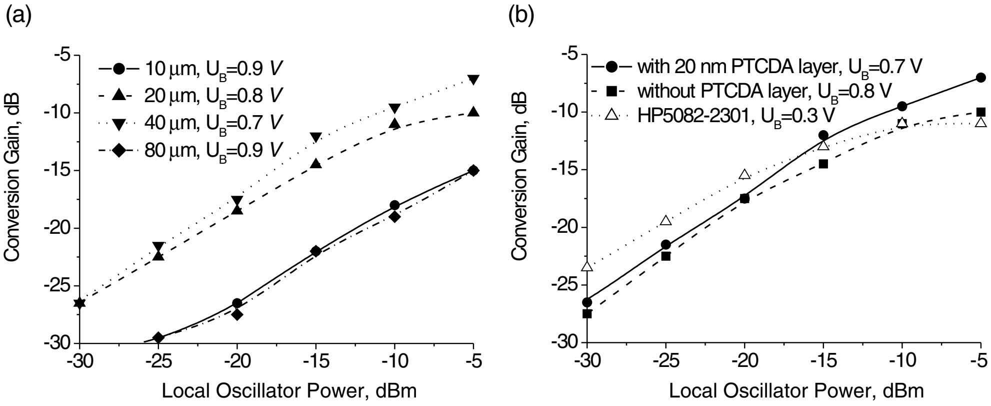

Figure 6. Mixing efficiency of OI diodes (a). Comparison to a reference sample without a PTCDA layer and a conventional Schottky diode (b).

organic semiconductor and organic–inorganic interface play an active role in the mixing, since it is achieved at lower optimum bias voltages. An additional reduction can be achieved by deposition of a thinner organic layer [2] and optimizing the substrate treatment before PTCDA deposition. Sulfur, selenium or halogen passivation of the GaAs surface have been discussed in this context [12–15]. The CG values obtained for both groups of samples are comparable to these for a conventional Schottky diode (HP5082-2301) measured under the same experimental conditions. Our non-optimized devices containing a PTCDA layer show 3 dB larger CG at high P_{LO} compared to Ag/GaAs diodes.

6. Conclusions

Heterostructure Ag/PTCDA/GaAs Schottky diodes have been characterized in the frequency range from 50 to 2000 MHz and their basic parameters have been extracted. Organic–inorganic devices have been compared with reference samples with the same geometry but without a PTCDA layer. It was shown that organic material enhances the mixing characteristics of the Schottky diodes by lowering the junction capacitance and restricting the current flow through the sample. Future investigations will be performed with GaAs material with different doping concentrations and different thickness of the organic layer.

Acknowledgment

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