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Growth and Characterization of Organic Semiconductor Devices: Photodetectors and Light Emitting Diodes (OLEDs)

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We discuss growth, characterization, and optimization of photodetectors and light emitting diodes (OLEDs) based on organic semiconductors. Thin film devices are fabricated by depositing organic source materials on cooled substrates under ultrahigh vacuum condition. This growth technique allows to achieve reproducible layer thickness and to optimize device performance. PTCDA-on-GaAs photodetectors show breakdown voltages exceeding 100 V, dark current densities as low as $5 \cdot 10^{-6}$ A/cm^2, and a frequency limit of 5 GHz. Multilayer OLEDs with an internal quantum efficiency of 5.5 % and a maximum optical output power of 0.3 mW are presented.

1. Introduction

Optoelectronic and electronic devices based on organic semiconductors have been successfully fabricated over the last decade. Among the variety of organic thin film devices, organic-on-inorganic heterostructures[1], waveguides[2], and multilayer organic light emitting diodes (OLEDs)[3] are of great interest for photonic systems and future display applications. In this paper, we report on growth, preparation, and characterization of fast PTCDA-on-GaAs photodetectors and discuss growth and optimization of single and double heterostructure OLEDs.

2. Growth and Technology

Organic semiconductors are reproducibly deposited under ultrahigh vacuum (UHV) conditions at base pressures of less than 10^{-8} Torr. This growth technology is well known from the molecular beam epitaxy (MBE) of III/V compound semiconductors. Organic source materials are evaporated from effusion cells provided with mechanical shutters. The growth rate is controlled with a quartz thickness monitor and can be adjusted to deposite even molecular monolayers with 0.1 nm/s. Film thicknesses and layer morphology can be optimized and lead to improved device performance. In contrast to the conventional MBE process, the weak van der Waals forces between the molecules require that the substrates be kept at room temperature or even cooled down to 77 K during growth. In addition, organic layer sequences can be grown on nearly arbitrary substrates since lattice matching is not necessary.

The arrangement of our UHV organic molecular beam deposition (OMBD) system depicted in Fig. 1 follows the concept of conventional MBE systems. It consists of a chamber for the deposition of organic semiconductors (OMBD 1) provided with four effusion cells, a preparation and metallization chamber, a sputter chamber, a II/VI-MBE chamber and a load lock module. An enhanced OMBD chamber with up to eight effusion cells is under construction. The chambers are connected by an UHV transfer system. This setup allows to deposit subsequent layers of inorganic semiconductors, various organic semiconductors, metallic contacts, ITO (indium-tin-oxide) transparent contacts, and dielectric films under permanent high vacuum conditions. Therefore, degradation of the surface due to exposure of the devices to the ambient enviroment is avoided during the growth process. Standard lithography and lift-off techniques can be used for pattern definition. In addition, the organic semiconductor layers have to be passivated with thin inorganic films.

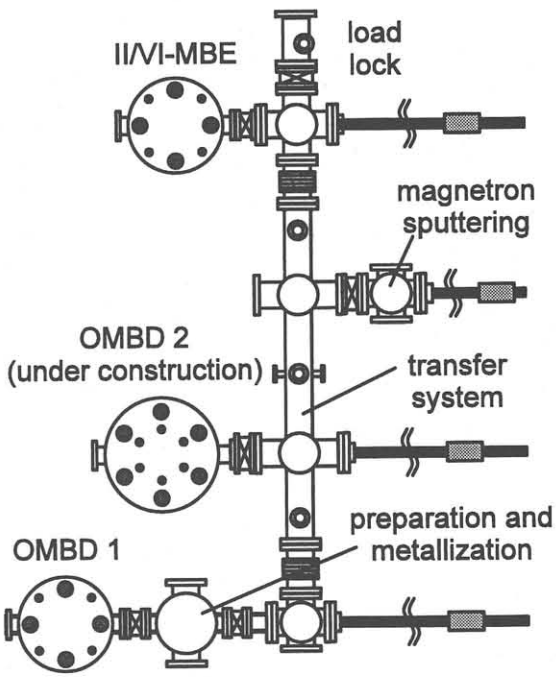

Fig. 1: Organic molecular beam deposition system (OMBD).

3. Photodetectors

Organic semiconductors are promising for the design of integrated devices on III/V semiconductors or on silicon due to the low substrate temperatures which avoids thermal degradation of already processed devices. We report on PTCDA-on-GaAs photodetectors as an example for an application of organic-on-inorganic semiconductor heterostructures. The molecular structure of PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) is shown in Fig. 2.

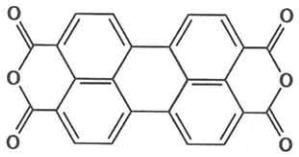

Fig. 2: Molecular structure of PTCDA.

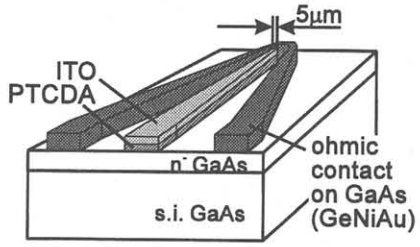

Fig. 3: PTCDA-on-GaAs photodetector.

For the design of the PTCDA-on-GaAs heterostructure photodetector a lateral concept similar to MSM (metal-semiconductor-metal) detectors is used (Fig. 3). In contrast to conventional MSM detectors, one of the metal contacts is substituted by a 100 nm thick transparent PTCDA contact. This allows to transmit the incident light through the large area contact into the absorbing depletion region of the n^--GaAs epitaxial layer. Using thicknesses of $\lambda/4$, these layers also serve as anti-reflection coating. To reduce the resistance the outer ohmic contact consists of alloyed Ge-Ni-Au layers. For on-waver probing the signal-ground-signal configuration is tapered to a tip of 5 μm width. ITO (tin doped indium oxide) is sputtered on top to improve the lateral conductivity. Furthermore, ITO surves as passivation layer during the lithography process. As depicted in Fig. 4, these organic-on-inorganic semiconductor heterostructures exhibit breakdown voltages exceeding -100 V and dark current densities as low as $5 \cdot 10^{-6}$ A/cm^2.

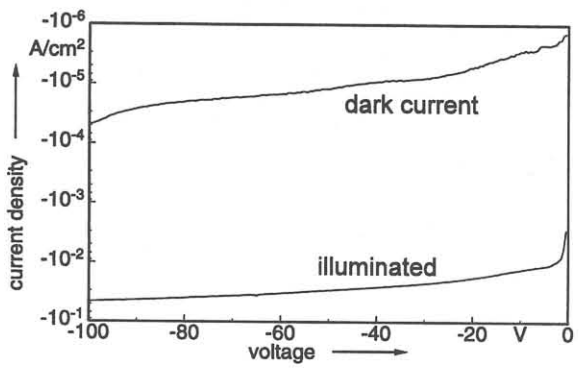

Fig. 4: Current density-voltage characteristics.

For ultrafast time domain measurements the device was excited by 100 fs pulses of a mode locked Ti:Sp laser at a wavelength of $\lambda = 830$ nm. The pulse response shown in Fig. 5a) exhibits a full width half maximum (FWHM) time of 40 ps. The corresponding Fourier transform leads to a 3 dB frequency limit of 5 GHz (Fig. 5b).

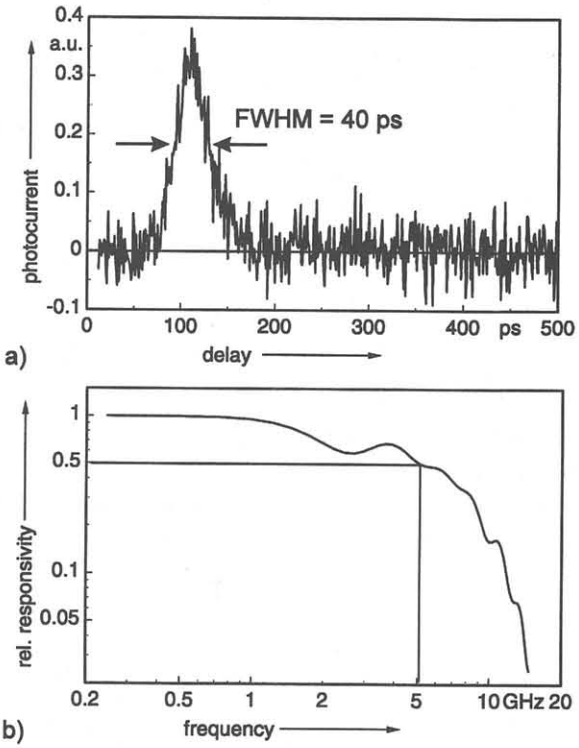

Fig. 5: (a) Pulse response and (b) Fourier transform of pulse response of a PTCDA-on-GaAs photodetector.

4. Organic Light Emitting Devices (OLEDs)

Multilayer OLEDs allow to achieve bright electroluminescent emission in the visible spectral region at low driving voltages[4]. Fig. 6 shows the layer sequence of single and double heterostructure devices suited for full color flat panel displays. Electrons injected from the Mg/Ag top contact and holes injected from the ITO substrate reach the emission layer through electron and hole transport layers, respectively, and recombine generating singlet excitons that decay radiatively with emission in the visible spectral region.

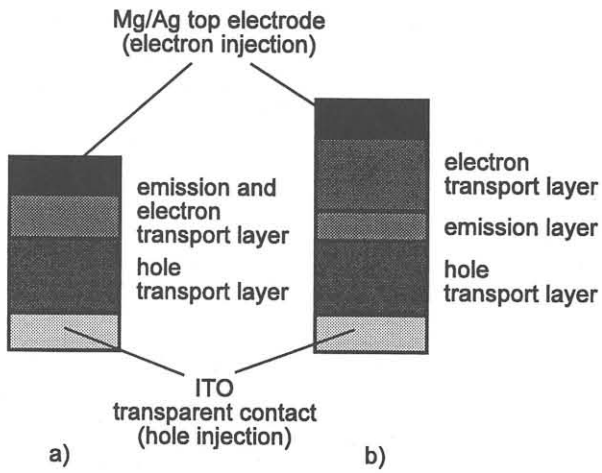

Fig. 6: Layer sequence of (a) single and (b) double heterostructure OLEDs.

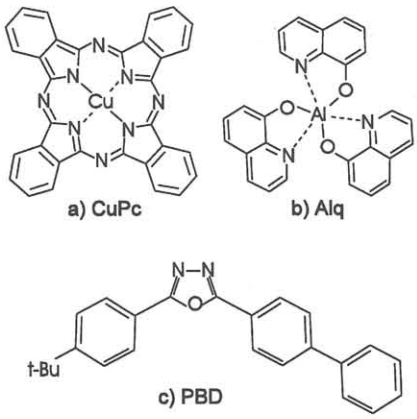

Fig. 7: Molecular structures of (a) CuPc, (b) Alq, and (c) PBD.

The metal-organic complex CuPc (copper phthalocyanine) exhibits preferentially hole-transporting properties, whereas the 1,3,4-oxadiazole-derivative PBD (2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole) serves as electron transport layer. Emission in the green spectral region (λ_{peak}=530 nm) is obtained by choosing the highly fluorescent metal-chelate complex Alq (tris-(8-hydroxychinoline) aluminum) as emission layer. The moledular structures of the organic semiconductors are shown in Fig. 7. Multilayer sequences are grown on transparent ITO coated glass slides with a sheet resistance of 120 $\Omega/\square$. Optimum growth rates of 25 – 80 Å/min and low substrate temperatures allow to achieve smooth thin films. The top electrode consists of a circular, 2 mm diameter, 200 nm thick Mg contact defined by a shadow mask. The Mg layer is reinforced by 200 nm Ag to protect the electrode from atmospheric oxidation.

Emission in the green spectral region is achieved under cw-operation at room temperature and normal ambient conditions. A large area Si photodetector is used to measure the optical output power of the surface emitting device. However, only about 8.4 % of the generated radiation contributes to the detected optical power due to total reflection at the interfaces, absorption in the CuPc layer, and the aperture limit of the photodetector.

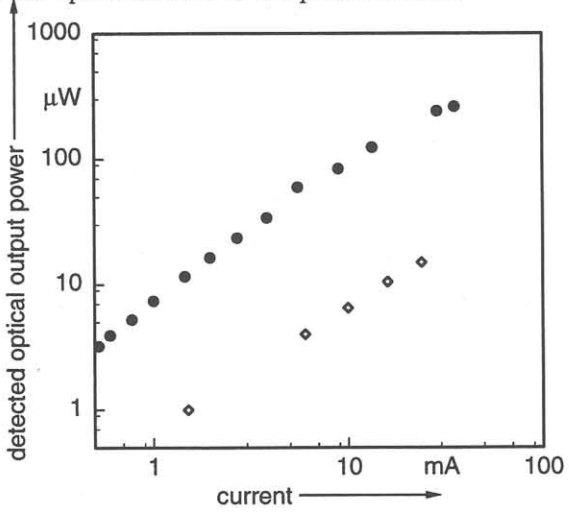

Fig. 8: P-I characteristics of single (◇) and double (•) heterostructure OLEDs.

The optical output power-current (P-I) characteristics of single (◇) and double (•) heterostructure OLEDs with a contact diameter of 2 mm are compared in Fig. 8. The optical output power depends nearly linearly on the injected current. A maximum estimated internal quantum efficiency of 0.4 % and a maximum optical output power 35 μW are obtained for a single heterostructure device with a 40 nm thick Alq layer and a 60 nm thick CuPc layer. The optimized double heterostructure device composed of 30 nm CuPc, 80 nm Alq, and 30 nm PBD shows a maximum detected optical output power of 270 μW and an estimated internal quantum efficiency of 5.5 %, which is by a factor of ten larger than the value for single heterostructure devices due to an improved confinement of the molecular excitons and an enhanced overlap of electron and hole densities within the emission layer. The influence of the Alq layer thickness on the quantum efficiency is indicated in Fig. 9.

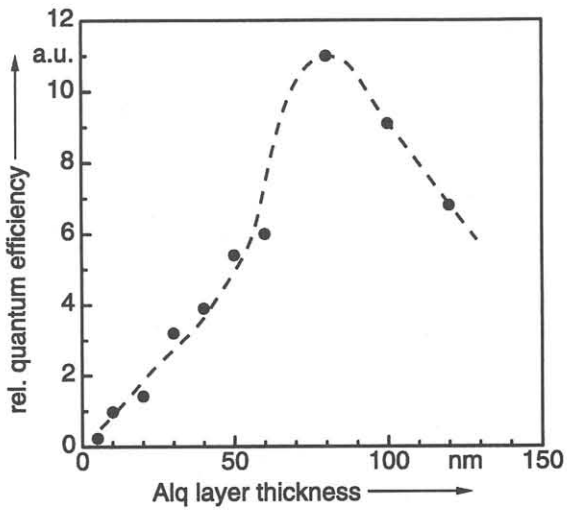

Fig. 9: Quantum efficiency of a double heterostructure OLED as a function of the Alq layer thickness.

5. Summary

Photonic devices based on organic semiconductors have been successfully fabricated. The OMBD technique allows to grow organic thin films with high reproducibility and to optimize device performance. PTCDA-on-GaAs photodetectors show breakdown voltages exceeding 100 V, dark current densities as low as $5 \cdot 10^{-6}$ A/cm^2, and a frequency limit of 5 GHz. Multilayer OLEDs for the green spectral region with an estimated internal quantum efficiency of 5.5 % and a maximum optical output power of 270 μW have been obtained.

References

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