

Characterization of Organic Semiconductors and Conductors by Means of Conductivity and Field Effect Using the Example of Graphene

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Summary:

For the first time novel water-based graphene flake solution was deposited on substrates with an interdigital ITO/gold-electrode design. The electrical properties before and after thermal annealing at 120 °C were investigated and the deposition method was evaluated with different dilution concentrations. The graphene thin film was investigated with AFM measurements. The substrates and the measurement setup allowed the characterization of the deposited graphene solution. Further examination of contact resistance and layer deposition methods is needed.

Keywords: organic field effect transistor, graphene, deposition, semiconductor, electrical characterization

Background, Motivation and Objective

Since the discovery of organic light-emitting diodes (OLEDs) by Tang, an infinite number of organic semi-conductive materials have been developed. They have found their way into our daily lives as OLED displays, whether in smartphones or televisions [1]. There are now a number of conductive organic materials, such as PEDOT:PSS or graphene. One challenge for the commercial application of these materials is their reproducible production and deposition. Analytical methods of organic chemistry often reach their limits or are not applicable. Therefore, electrical analysis methods, such as the measurement of conductivity or field effect characteristics, are of high interest. Thus, focus of this work are chip-based substrates with specific electrode structures, that can be used for the development and evaluation of materials. A common example for the characterization of organic semiconductors is the determination of the charge carrier mobility of organic material. This can be done by measuring the field effect of an organic field effect transistor (OFET). The Fraunhofer IPMS has developed various OFET test substrates that enable the electrical evaluation of materials. The applicability of the implemented structures as a test platform is demonstrated by using a commercial graphene flake formulation as an example.

Graphene is considered a promising candidate for future nano-electronics due to its exceptional electrical properties. As an additional monolayer

it is able to improve function, for example to reduce drift in ISFET based pH sensors or allow the detection of certain ions for sensor applications [2 - 4].

The challenge is the homogenous deposition of graphene solutions at low temperatures. For example, chemical vapor deposition (CVD) can achieve temperatures as low as 300 °C [5].

Description of the New Method or System

For the first time water based graphene flake solution (E-Graphene Dispersion G-DISP-H2O-CSO, Fa. Sixonia Tech GmbH, Dresden, Germany) was dispensed onto test substrates to investigate the electrical properties.

The test chips (OFET substrates, AX1579, Fraunhofer IPMS Dresden, Germany) described in Figure 1 are 15x15 mm² in size and usually have 16 source-drain interdigital electrodes made of gold, which are arranged on the gate oxide, typically SiO₂, via an ITO (Indium-tin-Oxide) adhesive layer. The underlying n-doped silicon of the wafer was used as a gate electrode. For different requirements, different channel lengths and widths are available, e. g. to determine the contact resistances.

This electrode arrangement can be used, for example, to determine the conductivity of the organic material by applying a voltage between the source and drain electrodes. In the case of semiconductor materials, the gate electrode can also be used as a control element, that affects the

field effect. The charge carrier mobility can then be determined from the characteristic transistor curves. This material-dependent parameter which is an indication of the usability of the tested material. The measured material properties are influenced by the material purity, the deposition conditions and the substrate itself. Both the conductivity and the charge carrier mobility are therefore suitable for monitoring the material quality and the deposition conditions. The used test substrates allow standardized material characterization due to their reliability and reproducible preparation.

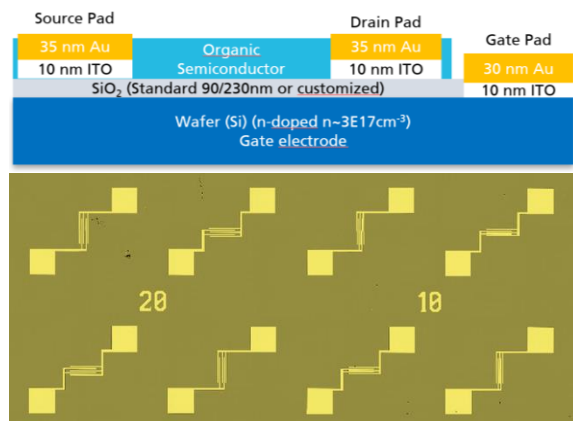


Figure 1: Top: Cross-section of an OFET (not to scale); bottom: investigated source-drain interdigital electrode arrays of different arrangement and channel dimensions prior to deposition, with removed protective coating; situated on a 15x15mm² OFET test chip

A process for structured deposition on OFET test substrates was developed for the graphene formulation. The graphene solution allowed easy application (Figure 2) and offered the advantages of organic electronics, such as low energy input at room temperature and low manufacturing costs compared to pure silicon-based technologies like CVD.

After removing the protective coating AR PC 5000/3.1 from the OFET substrates, the graphene solution with graphene flakes was applied by means of stamps using a fine dispenser (HÄCKER AUTOMATION GmbH, Waltershausen, Germany). A stamping process was introduced to ensure reproducible production. The graphene solution was applied to the 16 transistor structures of each OFET chip using the fine dispenser and a specially manufactured stamp attachment.

The OFET-test substrates of type AX1579, n-doped silicon, 230 nm SiO₂ gate oxide. The test structures consist of channel lengths, that is defined by the distance of the electrodes, ranging from 10 μm to 80 μm and channel width of 2 mm.

The layers obtained were examined electrically and optically. In addition to methods for

determining the layer roughness, such as atomic force measurements (AFM), microscopic analyses of the distribution and height of the graphene flake layer and an electrical characterization with two Keithley 236 source measurement units (SMUs) were carried out to determine the conductivity of the material, among other things.

The silicon bulk is the gate electrode but was not used in the measurements. The OFETs were connected to the measuring system using needle contacts.

The measurements were carried out at room temperature before and after thermal annealing of the chips at 120 °C in an industrial oven.

Images were taken with a digital camera, an Olympus digital microscope DSX1000 and the channel height was measured with a Keyence VK-X200 laser microscope.

Results

The graphene solution was dispensed about three months after production and measured electrically. AFM measurements were performed additional three months after deposition. The solution was not diluted. The deposition process showed good results in terms of positioning. The whole electrode area was covered.

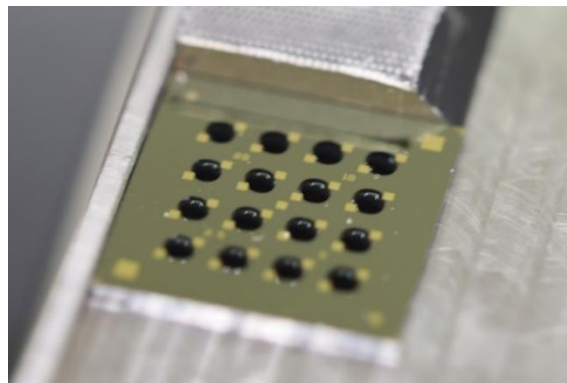


Figure 2: Top: Straight deposited wet graphene solution on the OFET test chip

The fresh graphene solution with up to 2 mg/ml graphene was fabricated less than one week before the deposition. Thus, no agglomerates of graphene flakes and a uniform film were expected.

Different states of graphene solution were investigated: pure graphene with an age of three months and fresh graphene diluted with ultrapure water (0,055 μS/cm at 24,1 °C UV/TC, Thermo Scientific Barnstead GenPure) in the ratio 1:7. In Figure 3 an example of the deposition can be seen. Evaporation happened within five minutes after deposition, supported by the air flow in the clean room.

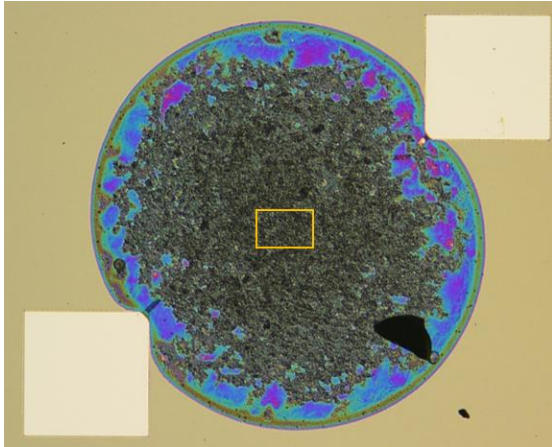


Figure 3: Microscope image of graphene on OFET substrate with three months old graphene water solution, untreated

First atomic force measurements (Figure 4) show a rather random orientation and a very thick graphene layer.

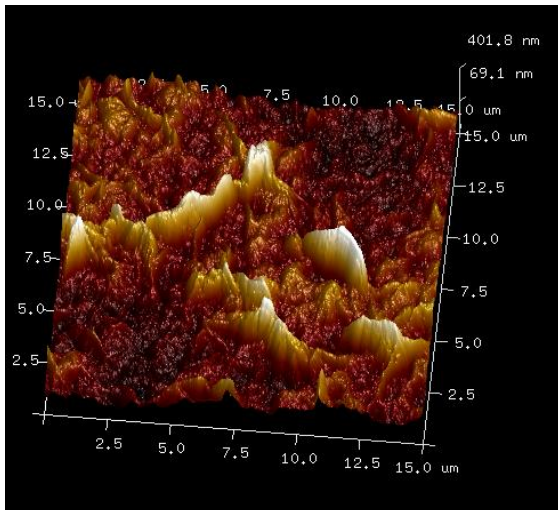


Figure 4: AFM measurement of graphene on OFET substrate with three months old graphene water solution; untreated

As can be seen in the AFM imaging, the agglomeration due to the age and treatment of the solution had a negative effect on the graphene layer. Graphene flakes seem to be oriented not only horizontally, but also vertically.

The resistance from the slope of the I-V measurement for the average curve (Figure 6) was calculated by averaging the four OFETs of the same channel length ($w = 10 \mu\text{m}$ and $20 \mu\text{m}$).

The layer thickness of about up to $15 \mu\text{m}$ on average was roughly estimated from laser microscope measurements by measuring the average height along a straight line across a homogeneous part of the OFET.

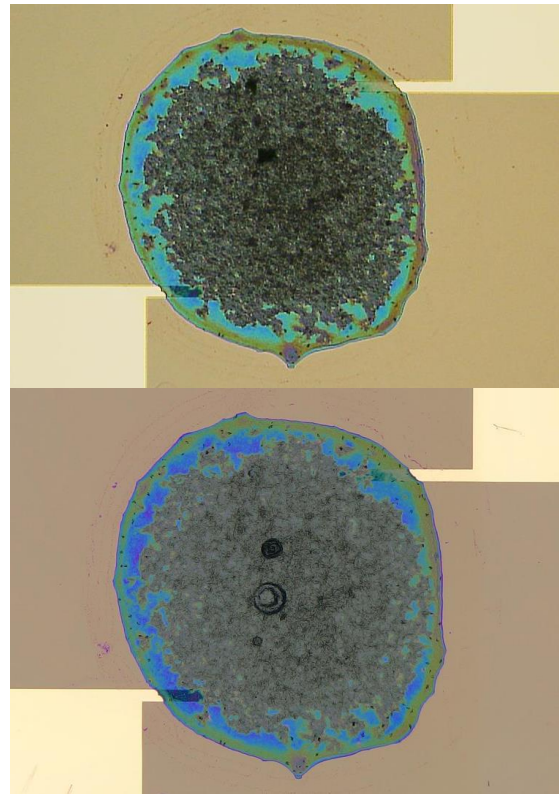


Figure 5: Graphene on OFET substrate with three months old graphene water solution, untreated (top) and tempered at $120 \text{ }^\circ\text{C}$ for 17 h (bottom)

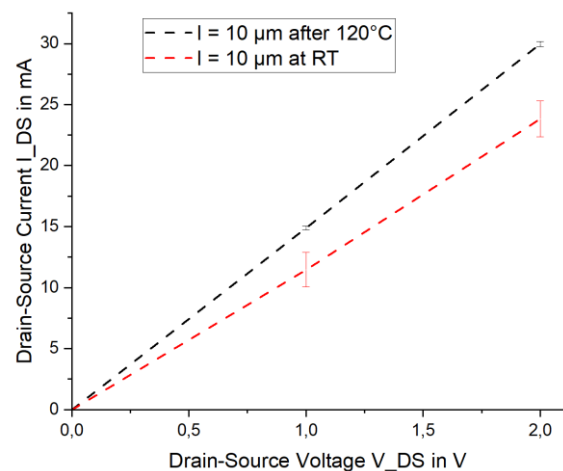


Figure 6: Average I-V curves I_{DS} vs. V_{GS} with standard deviation for four OFET substrates with $10 \mu\text{m}$ channel length and $2000 \mu\text{m}$ channel width at room temperature (RT) and after tempering for 17 h at $120 \text{ }^\circ\text{C}$

Thermal annealing for 17 hours at $120 \text{ }^\circ\text{C}$ led to a decreased resistance. The resulting I-V curves for $w = 20 \mu\text{m}$ are very close to the $10 \mu\text{m}$ channel length OFETs. Since the channel length does not appear to have any influence, it had to be assumed that the contact resistance between graphene and the gold electrodes was larger than the graphene layer resistance and therefore interfered with the measurement of the latter.

Alternatively, the graphene was perhaps just deposited on top of the OFET electrodes and contact due to anisotropy is only possible in a relatively poorly conductive direction through the material and not through an electrically continuous layer. The entire thickness of the material may not be used at all.

Because older graphene solution is likely to form agglomerates that could have led to such an unpredictable behavior, first trials with fresh graphene solution, that was diluted with ultrapure water in a ratio 1:7 followed. AFM measurements showed a thinner and more homogenous graphene layer about one week after deposition (Figure 7). A lower roughness Rms (Rq) of 11 nm was achieved compared to about 20...90 nm for the three months old graphene solution.

First optical measurements of the graphene layer also showed a much smaller estimated thickness (up to 4 μm) which resulted in the electrodes being visible (Figure 7).

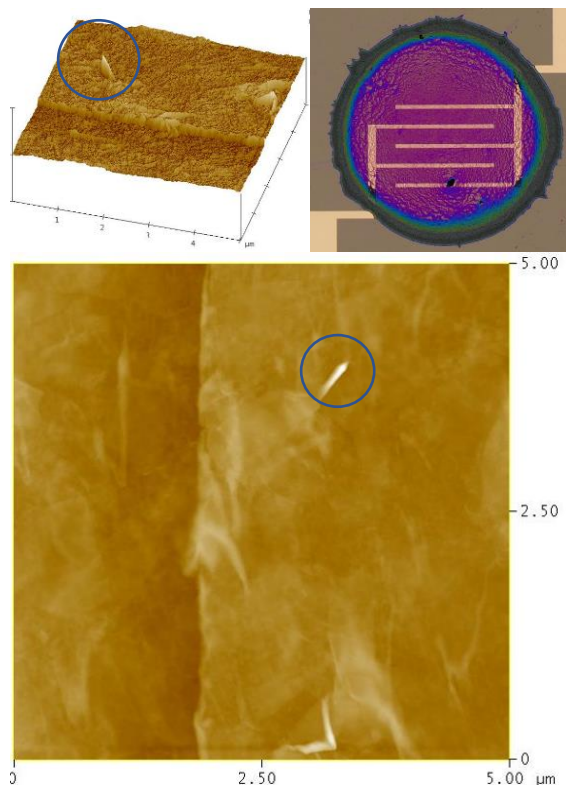


Figure 7: top left: 3D view of the scan with highlighted flake; top right: top view via microscope; bottom: AFM measurement top view of fresh graphene, diluted with ultrapure water in a ratio 1:7; untreated; the OFET substrate electrode edge is visible

Initial single measurements of OFETs with channel lengths of 10 μm , 20 μm and 80 μm showed larger differences in resistance (Figure 8).

First estimates of the conductivity led to the same order of magnitude of about 0,1 S/cm for

both graphene solutions. The results show a much smaller conductivity than stated in the datasheet (>500 S/cm).

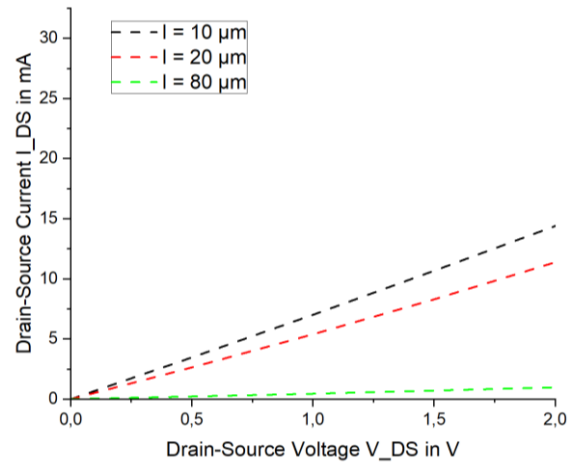


Figure 8: I-V curves I_{DS} vs. V_{GS} of on three single measurements of fresh graphene solution on OFET substrate of the same type with channel lengths of 10 μm , 20 μm and 80 μm

The assumed layer thickness is a variable influencing this value. Thus, the two graphs shown can't be directly compared for evaluation of the conductivity. The relevance of edge effects of the interdigital structures couldn't be determined. This was due to the lack of detailed knowledge about the wetting of the substrate surface by the graphene flakes.

Because the characterization of such materials is influenced by multiple factors, like age and agglomeration of the solution, as well as wetting behavior, the results shown are first estimate for a simple deposition method and the capabilities of OFETs for characterizing materials.

In order to evaluate the conductivity and contact resistance, the graphene orientation and the layer thickness must be measured precisely.

Summary and Outlook

Overall, the OFET substrates and the measurement setup allow the characterization of the deposited graphene solution.

Follow-up investigations will focus on utilization of more precise deposition methods like spray coating which are expected to provide a smaller and more flat deposition of the graphene flakes.

Furthermore, dilution with ethanol will be investigated. It is assumed to improve the wetting behavior and increasing conductivity by reducing surface tension and improving graphene flake orientation. Additionally, OFETs with heating elements will be used, to investigate the influence if temperature on the conductivity in more detail.

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