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TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics – Part 5-3: Thin-film organic/nano electronic devices – Measurements of charge carrier concentration

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NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

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Technical Specifications are subject to review within three years of publication to decide whether they can be transformed into International Standards.

IEC TS 62607-5-3, which is a Technical Specification, has been prepared by IEC technical committee 113: Nanotechnology for electrotechnical products and systems.

The text of this Technical Specification is based on the following documents:

Draft TS	Report on voting
113/477/DTS	113/523/RVDTS

Full information on the voting for the approval of this Technical Specification can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC TS 62607 series, published under the general title *Nanomanufacturing – Key control characteristics*, can be found on the IEC website.

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- transformed into an International Standard,
- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

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INTRODUCTION

Organic/nano thin-film devices are attracting much attention as promising candidates for light, low cost, flexible, and printable devices in large-area electronics applications. Recently, charge carrier doping techniques have been intensely studied and developed, in the same way as the mature silicon technologies. In organic light-emitting diodes (OLEDs) and organic thin-film transistors (OTFTs), which are typical organic/nano thin-film devices, carrier doping around contact electrode regions with molecular donor/acceptor dopants are often utilized to make ohmic-like contacts for the purpose of increasing electric current in the devices. While the great importance of carrier doping in organic/nano layers is well recognized, the carrier doping mechanisms have not been fully understood yet, and the evaluation method of charge carrier concentration in these materials has not been established.

Conventional representative methods for evaluating charge carrier concentrations (or dopant concentrations) and the type of charge carrier (electron or hole) in inorganic semiconductor materials are Hall-effect measurements and capacitance-voltage measurements. For example, the Hall-effect measurement based on the van der Pauw configuration enables one to get the above-mentioned physical parameters of the charge carrier in specimens with arbitrary shapes including thin-film structures. However, this versatile method cannot be utilized for higher resistance materials such as low-mobility organic semiconductors because of lower currents and sensitivities in the Hall effect. At the present time, the capacitance-voltage measurement based on metal/insulator/semiconductor structures is not applicable to highly-doped organic semiconductors that show some level of metallic behaviour. Therefore, standard methods and guidelines for measuring charge carrier concentration in organic semiconductor layers need to be developed.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 5-3: Thin-film organic/nano electronic devices – Measurements of charge carrier concentration

1 Scope

This part of IEC TS 62607, which is a Technical Specification, specifies sample structures for evaluating a wide range of charge carrier concentration in organic/nano materials. This specification is provided for both capacitance-voltage (C-V) measurements in metal/insulator/semiconductor stacking structures and Hall-effect measurements with the van der Pauw configuration. Criteria for choosing measurement methods of charge carrier concentration in organic semiconductor layers are also given in this document.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1
doping
addition of impurities to a semiconductor to control hole or electron concentrations

Note 1 to entry: For organic semiconductors, not only atomic, but also molecular impurities are utilized.

Note 2 to entry: The added impurities are called "dopants".

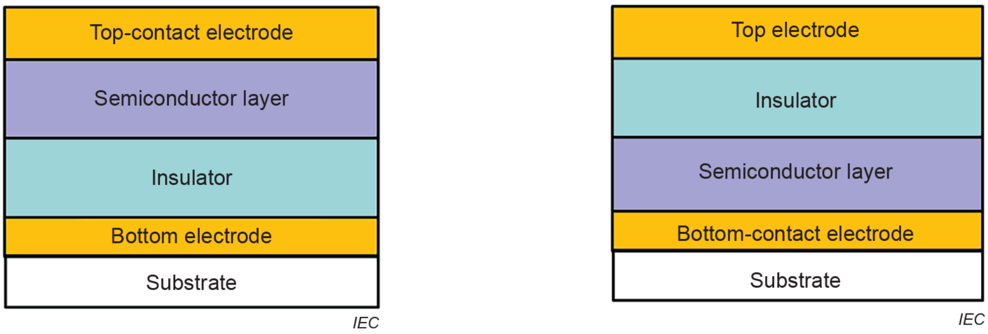
3.2
bottom-contact electrode
contact electrode located underneath the semiconductor layer to be tested

3.3
top-contact electrode
contact electrode located on top of the semiconductor layer to be tested

4 Sample structures

4.1 Metal/insulator/semiconductor (MIS) structure

Fabrication of a metal/insulator/semiconductor (MIS) structure as shown in Figure 1 is necessary for measuring a capacitance-voltage (C-V) curve in organic/nano semiconductor layers. This structure consists of a series capacitor of the insulator and a depletion region in the semiconductor layer.



a) Top-contact configuration b) Bottom-contact configuration

Figure 1 – Typical metal/insulator/semiconductor (MIS) structures

However, C-V measurements for MIS structures made of an identical semiconductor material provide various values of carrier concentration according to the difference in the sample structures (see Annex A, Clauses A.2, A.3 and A.4). Accordingly, the measurement of the carrier concentration with C-V measurements largely depends on the extrinsic effects derived from structure and electronic properties of the semiconductor layer itself and the metal/semiconductor interface region. Therefore, the following issues shall be considered for preparing MIS structures for reliable C-V measurements (Figure 2).

1) Quasi-ohmic contacts between the semiconductor layer and the metal electrode shall be formed. For example, contact doping is one of the practical techniques for this purpose.
2) For suppressing hysteresis phenomena in the measured C-V curves, the insulator in the MIS structure shall be as thin as possible, while maintaining good insulating properties.

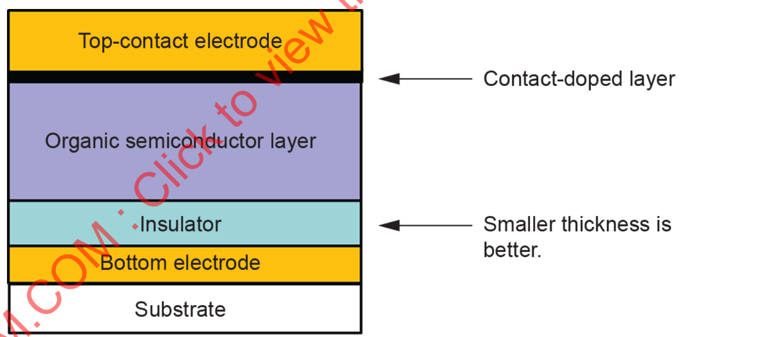
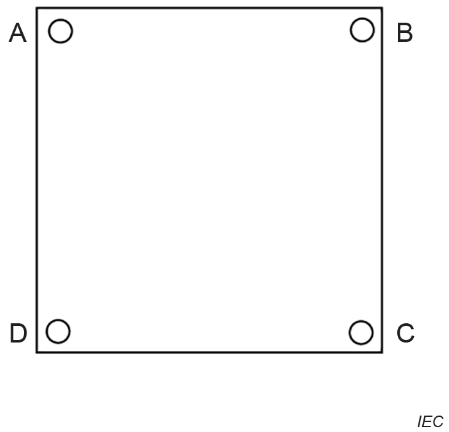


Figure 2 – An organic MIS structure favourable for capacitance-voltage measurements

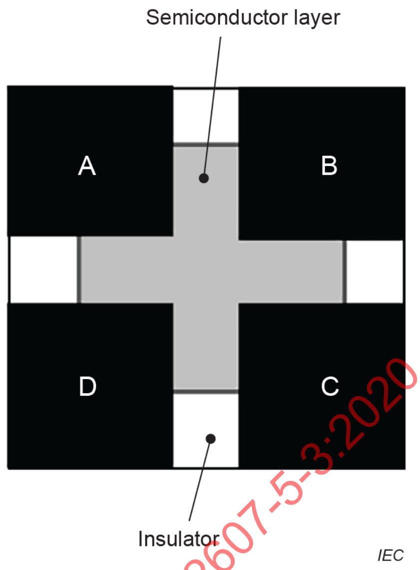
4.2 Thin-film specimens with the van der Pauw configuration

Thin-film specimens with the van der Pauw configuration as shown in Figure 3 can be considered for Hall-effect measurement in highly-crystalline organic/nano materials.

Figure 3a) shows the conventional van der Pauw configuration with four point contacts at the corners of the square film specimens, where the distances between individual contacts are on a centimetre or millimetre scale. However, this versatile method cannot be applicable to higher resistance materials such as organic semiconductors because of lower currents and sensitivities in Hall effect. Therefore, an electrode structure with a micro-scale gap between diagonally opposite electrodes can be an alternative way for enabling Hall-effect measurement in an organic semiconductor layer as shown in Figure 3b). In this case, quasi-ohmic contacts between the semiconductor layer and the metal electrode shall be formed.



a) Typical sample structure



b) Example of a sample structure with top-contact electrodes

Figure 3 – Sample structures for Hall-effect measurement with the van der Pauw configuration

5 Criteria for choosing a method for measuring carrier concentration in organic semiconductor layers

Criteria for choosing a method for measuring carrier concentration in organic semiconductor layers are proposed as follows. Capacitance-voltage measurements are suitable for organic thin films with carrier mobilities lower than approximately 1 cm^2/Vs, while both Hall-effect measurements with van der Pauw configuration and capacitance-voltage measurements are considered to be available for organic thin films with carrier mobility higher than approximately 1 cm^2/Vs. The mobility of 1 cm^2/Vs has been regarded as the boundary value between band like transport region and hopping transport region [1][1]. The mobility can reach 1 cm^2/Vs to 10 cm^2/Vs in highly-crystalline thin films of some high-mobility organic semiconductors. However, values in the range of 10^{-5} cm^2/Vs to 10^{-1} cm^2/Vs in a large number of organic semiconductor thin films are not unusual because the mobility really depends on both the degree of order in molecular solids and extrinsic factors such as carrier traps and impurities [2].

6 Appropriate data formats

Examples of possible data formats for measurements of charge carrier concentrations in organic thin-film samples are given in Table 1 and Table 2. Items regarding measurement and sample conditions and results shall be included in these formats. Additionally, in the case of the Hall-effect measurements, it is highly recommended to show data plots on time variations of the measured Hall voltage against the polarity changes of the magnetic field.

[1] Numbers in square brackets refer to the Bibliography

Table 1 – Possible data format to be given together with carrier concentrations obtained with capacitance-voltage measurements

Item	Data
Measurement and sample conditions	Frequency of AC modulation voltage: [ ] Hz Amplitude of AC modulation voltage: [ ] V Sweep range of DC bias voltage: [ ] to [ ] V Measurement atmosphere: [ ] in a vacuum [ ] in an inert gas [ ] under ambient condition (relative humidity: [ ] %) Measurement temperature: [ ] K Active electrode area of the MIS structure: [ ] cm^2 Thickness of the active semiconductor: [ ] nm Dielectric constant of the active semiconductor: [ ]
Measurands	Majority carrier type: [ ] P-type [ ] N-type Carrier concentration: [ ] ± [ ] cm^{-3} Capacitance of insulator in the MIS structure: [ ] ± [ ] nF/cm^2 Hysteresis with DC bias sweep: [ ] No hysteresis [ ] With hysteresis (Hysteresis width: [ ] V)

Table 2 – Possible data format to be given together with carrier concentrations obtained with the Hall-effect measurements

Item	Data
Measurement and sample conditions	Kind of magnetic field: [ ] DC magnetic field [ ] AC magnetic field Amplitude of magnetic field: [ ] T Frequency of magnetic field: [ ] Hz (in the case of AC magnetic field) Amplitude of DC current: [ ] A Measurement atmosphere: [ ] in a vacuum [ ] in an inert gas [ ] under ambient condition (relative humidity: [ ] %) Measurement temperature: [ ] K Thickness of the active semiconductor: [ ] nm
Measurands	Majority carrier type: [ ] P-type [ ] N-type Carrier concentration: [ ] ± [ ] cm^{-3} Carrier mobility: [ ] ± [ ] cm^2/Vs Hall resistance: [ ] ± [ ] Ω Electrical resistivity: [ ] ± [ ] Ωcm

Annex A
(informative)

Case study of carrier concentration measurements of organic materials

A.1 Procedure of capacitance-voltage (C-V) measurement

Capacitance-voltage (C-V) curves for the MIS structure can be obtained by using a conventional impedance meter, which can apply a small AC voltage (V_{ac}) superimposed onto a DC bias (V_g) between the top and bottom electrodes of the MIS structure [3]. Figure A.1 presents the equivalent circuit model of C-V measurements for the MIS structure. The total series capacitance (C_{tot}) comprised by the insulator and the depletion region in the semiconductor layer is measured. A typical result of the C-V measurement is depicted in Figure A.2. The MIS structure shows two states according to the V_g value. One state is a depletion state which is empty of conducting electrons and holes in the semiconductor layer. The depleted semiconductor layer including ionized dopants (donors or acceptors) behaves like a capacitor. The other state is an accumulation state, in which conducting carriers are accumulated at the interface between the insulator and the semiconductor. The total capacitance of the MIS structure is increased due to the transition from the depletion to the accumulation state as shown in Figure A.2.

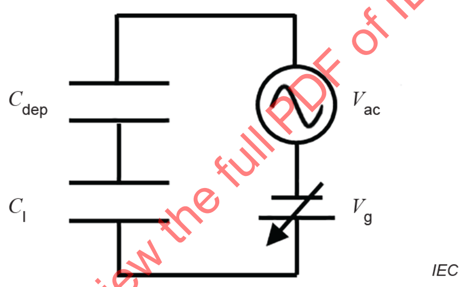


Figure A.1 – Equivalent circuit model for capacitance-voltage measurement with MIS structure

In the case of p-type semiconductors, at lower frequency and negative DC bias, the devices exhibit the capacitance of the insulator layer C_I due to the accumulation of holes. Sweeping to positive bias, C_{tot} drops monotonically as the semiconductor layer becomes depleted, as depicted in Figure A.2a). From that region, the majority carrier (hole) concentration N can be determined according to the standard theory on the MIS structure. In short,

$$N = \frac{2}{e\varepsilon_s\varepsilon_0 A^2 \left| \frac{\partial C_{tot}{}^{-2}}{\partial V_g} \right|} \qquad \text{(A.1)}$$

where

A is the active area of the MIS device;

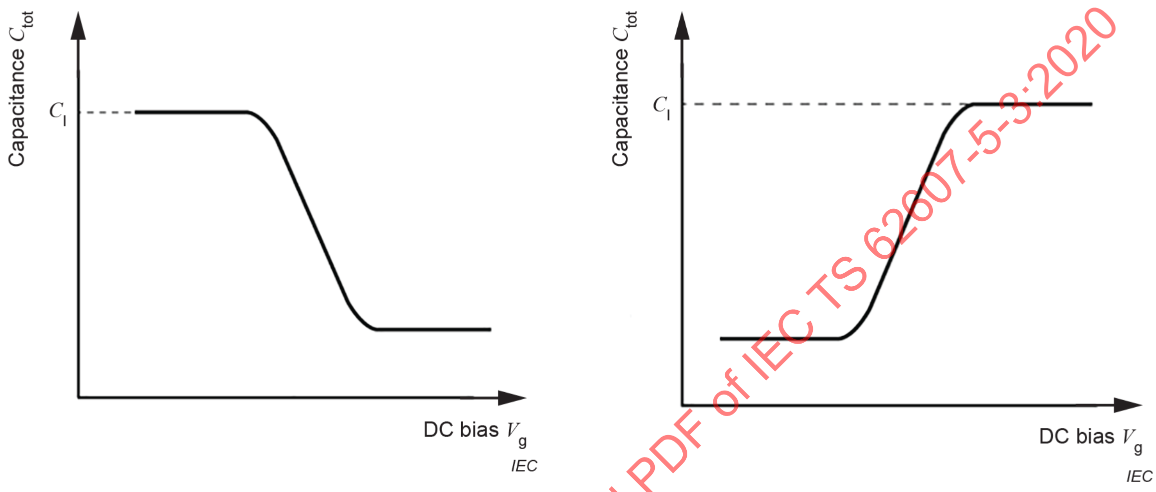
ε_s is the dielectric constant of the organic semiconductor materials;

e is the elementary charge;

ε_0 is the dielectric permittivity of vacuum;

C_{tot} is the total series capacitance comprised by the insulator and the depletion region in the semiconductor layer.

The value of $\left| \partial C_{tot}^{-2} / \partial V_g \right|$ is the slope of a least squares regression line obtained in the plot of $1/C^2 - V_g$ curve at the transient region from the depletion to the accumulation state. This procedure can also be applied to n-type semiconductor materials for evaluating electron concentration from C-V characteristics as shown in Figure A.2b).



a) **For p-type semiconductor materials** b) **For n-type semiconductor materials**

Figure A.2 – Typical capacitance-voltage curves observed for MIS structures with organic semiconductor films

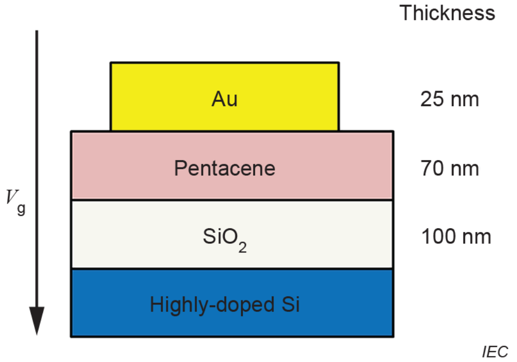
A.2 Capacitance-voltage measurement for unoptimized pentacene MIS structures

Clause A.2 describes some examples of C-V measurements for unoptimized pentacene MIS structures. Pentacene is one of the typical p-type organic semiconductor materials and is commercially available. Pentacene films usually show relatively small mobilities in the range from 0,01 cm^2/Vs to 0,1 cm^2/Vs (in the hopping transport region). There, Hall-effect measurements can not be used for evaluating carrier concentration of the pentacene thin films.

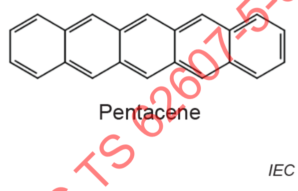
A MIS structure prepared for the C-V measurement is shown in Figure A.3a). Heavily doped silicon substrates (< 0,02 Ωcm, size: 1,5 cm × 1,5 cm) which have a 100-nm-thick thermally grown SiO_2 layer were employed as substrate. After cleaning them by sonication and vapour degreasing with ethanol, the wafers were treated with a UV ozone cleaner for 30 minutes, followed by surface passivation with octadecyltrimethoxysilane in gas phase. After removal of residues on Si substrates by sonication with organic solvents, the deposition of an active pentacene layer (thickness: 70 nm) onto the Si substrate was performed. Then, a 25-nm-thick gold top electrode was deposited by physical vapour deposition using a shadow mask pattern for circular electrode. The diameter of the Au top electrode was 1,0 mm.

The capacitance-voltage of the metal/insulator/semiconductor (MIS) structure was measured by an LCR meter with an internal DC voltage source. The modulation frequency and voltage for the measurements were 100 Hz and 100 mVrms, respectively. The C-V measurements were performed in a vacuum ($1{,}0 \times 10^{-2}$ Pa).

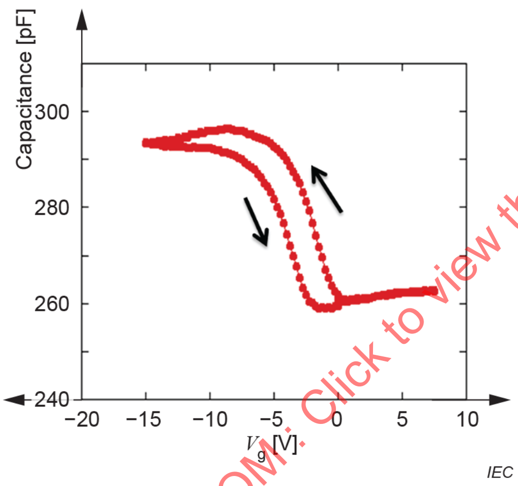
The capacitance-voltage curves obtained in this specimen are plotted in Figure A.3c), where the graphs show features of p-type semiconductors. This means that the total capacitance was increased with negative biasing, suggesting hole accumulation behaviours in the p-type pentacene thin film. The arrows in Figure A.3c) and d) indicate the bias-sweep direction. Typical injection-type hysteresis curves appear probably due to the carrier trapping in the pentacene layer and at the pentacene/SiO_2 interface.



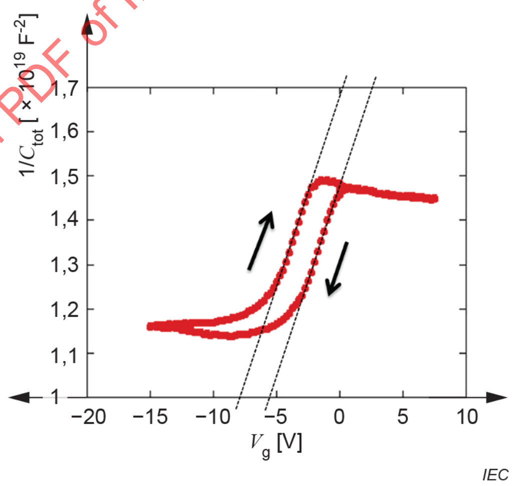
a) **Top-contact configuration**



b) **Bottom-contact configuration**



c) **Capacitance (C_{tot})-voltage (V_g) curve obtained for this sample**



d) **C_{tot}^{-2}-V_g plot calculated from the data shown in c)**

Figure A.3 – Capacitance-voltage curves obtained for the MIS structure with 70-nm-thick-pentacene film

The hole concentration of the pentacene thin film was evaluated by using Formula (A.1) with the following parameters: A = 0,95 mm^2, e = 1,602 × 10^{-19} C, ε_0 = 8,854 × 10^{-12} Fm^{-1}, ε_s = 3,0 according to the literature [4]. The dashed lines in Figure A.3d) showed the results of least-square fitting to the plots of 1/C^2 − V_g curves. The value of $\left|\partial C_{tot}^{-2}/\partial V_g\right|$, which was the mean value of the results measured with the forward and backward bias-sweep, was 9,5 × 10^{17} F^{-2}V^{-1}. Finally, the hole concentration was calculated to be 8,0 × 10^{17} cm^{-3}. In a previous work on the C-V characteristics of pentacene-based Schottky diodes, 3,1 × 10^{17} cm^{-3} was reported for undoped pentacene thin films [5]. However, the value obtained here is thought to be too large for undoped pentacene films, although unintentional hole doping with oxygen gases due to short-time air exposure can occur after the sample preparation.

A.3 Influences of semiconductor layer thickness and electrode contact conditions on C-V measurements

Clause A.3 reports the influences of semiconductor layer thickness and electrode contact conditions on C-V measurements for pentacene MIS structures.

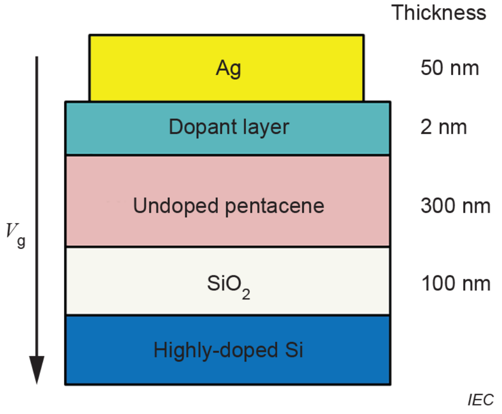
Thus far, Au top electrodes fabricated by vacuum deposition were used in many previous studies. However, during the Au deposition process, Au atoms with high thermal energy could result in damage of the organic semiconductor layers [6], [7]. For suppressing the degradation of the pentacene layer during the top electrode deposition, the top-electrode metal type was changed to silver (Ag), which has a lower evaporation temperature than Au. The thickness of the pentacene layer was also increased up to several hundred nanometres for the following two reasons:

1) the thicker semiconductor layer may be less sensitive to the damage caused by the deposited metal atoms;
2) the thickness of the semiconductor layer needs to be larger than its maximum depletion width.

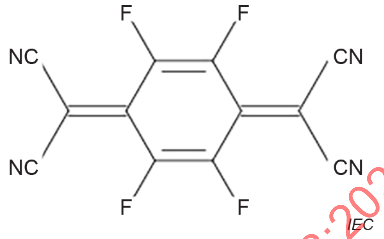
Quasi-ohmic contacts between the semiconductor layer and the metal electrode are also necessary to avoid undesirable formation of capacitance between the top-electrode and the semiconductor layer. Here, an acceptor dopant, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F4TCNQ), was employed in order to make quasi-ohmic contacts between the Ag electrode and the pentacene film.

The preparation of the pentacene MIS structure with interface dopant layers is as follows. Heavily doped silicon substrates (< 0,02 Ωcm, size: 1,5 cm × 1,5 cm) which have a 100-nm-thick thermally grown SiO_2 layer were employed as a substrate. After cleaning them by sonication and vapour degreasing with ethanol, the deposition of an active pentacene layer (thickness: 300 nm) onto the Si substrate was performed. Successively, an F4TCNQ layer with a thickness of 2 nm was deposited on top of the pentacene layer. Finally, a 50-nm-thick silver top electrode was deposited by physical vapour deposition using a shadow mask pattern for circular electrode. The parameters of the device structure are shown in Figure A.4. In addition, the MIS devices without F4TCNQ layers were also fabricated.

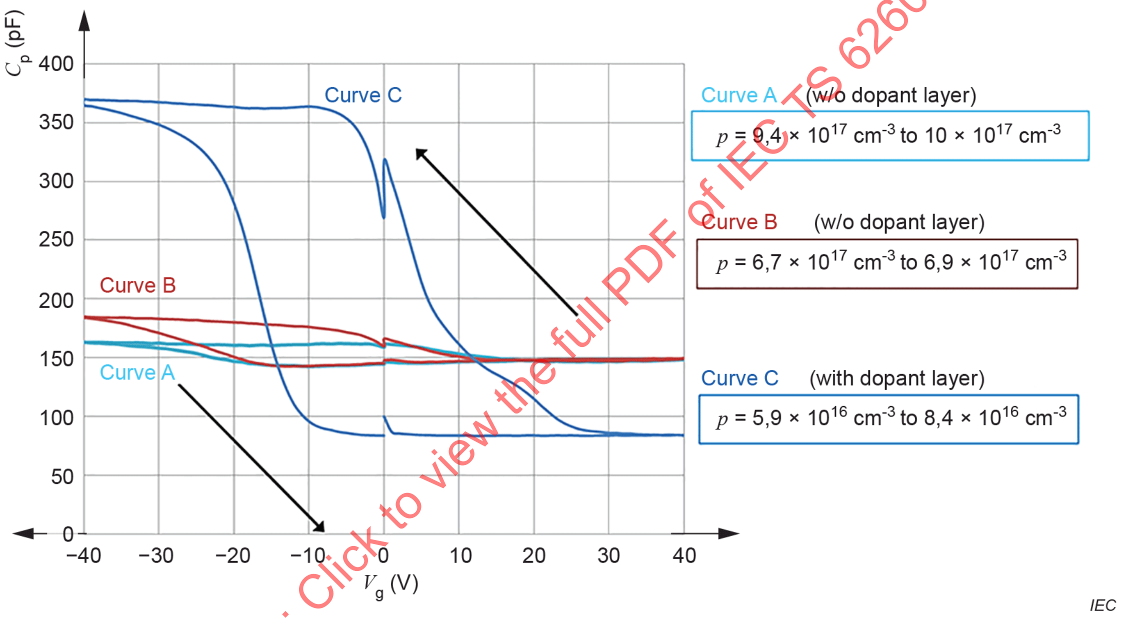
The capacitance-voltage measurements for the prepared structure were performed according to the same procedures as described in Clause A.2, except that the modulation voltage for the measurements was 50 mVrms. The measured capacitance-voltage curves are plotted in Figure A.3c). The arrows in Figure A.3c) indicate the bias-sweep direction. The shape of the curves was drastically changed probably due to the existence of the F4TCNQ layer and the larger pentacene film thickness, and the calculated hole concentration was decreased from $6{,}8 \times 10^{17}$ and $9{,}7 \times 10^{17}$ cm^{-3} to $7{,}2 \times 10^{16}$ cm^{-3} accordingly. In a previous work on a pentacene-based MIS structure, a value of 5×10^{16} cm^{-3} was also reported for an undoped pentacene thin film from the C-V measurement [8]. Therefore, it can be considered that improvements in the MIS structure can make the C-V measurement more reliable. However, injection-type hysteresis phenomena still appear obviously due to the carrier trapping, suggesting some room for further improvement in the pentacene MIS structure.



a) A pentacene MIS structure with an acceptor dopant layer



b) Molecular structure of an acceptor dopant (F4TCNQ)



c) Capacitance (C_{tot})-voltage (V_g) curve obtained for the pentacene MIS structure with and without F4TCNQ layers

Figure A.4 – Capacitance-voltage measurement examples for the MIS structure made of 300-nm-thick-pentacene film with and without contact doped layers

A.4 Capacitance-voltage measurement for a pentacene MIS structure with an ultrathin insulator

Clause A.4 reports experimental results of C-V measurements for pentacene MIS structure with an ultrathin insulator.

Hysteresis phenomena in C-V curves are caused by the trapping behaviours of charge carriers injected from the contact electrode into the semiconductor layer in the MIS structure, and tend to become more prominent in the larger voltage sweep range. Therefore, in order to make the C-V measurement feasible in the lower voltage sweep range, an ultrathin insulator made of aluminium oxide (AlOx) and alkylphosponic acid self-assembled monolayer (SAM) was employed for fabricating a pentacene MIS structure.

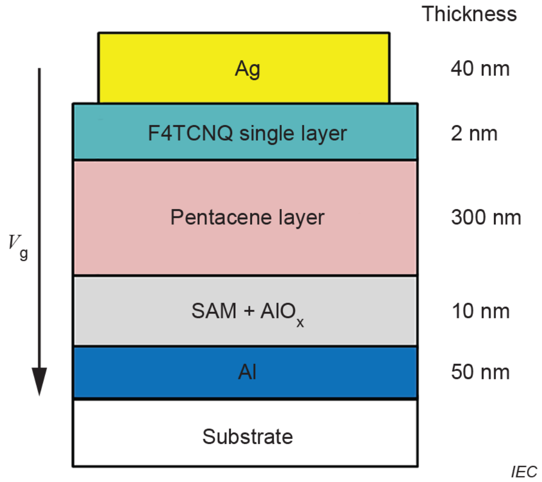
The preparation of the pentacene MIS structure with an AlOx layer is as follows. A 50-nm-thick aluminium film was deposited onto a Si substrate by sputtering method. Then, the Al surface was treated with oxygen plasma, resulting in the formation of an 8-nm-thick AlOx film on the aluminium bottom electrode. Then, tetradecylphosphonic acid (TDPA) SAM was fabricated on AlOx film surface. After that, the deposition of an active pentacene layer (thickness: 300 nm) was deposited onto the SAM-modified AlOx film surface. Successively, an F4TCNQ layer with a thickness of 2 nm was deposited on top of the pentacene layer. Finally, a 40-nm-thick silver top electrode was deposited by physical vapour deposition using a shadow mask pattern for circular electrode. A schematic drawing of the sample structure is shown in Figure A.5.

The capacitance-voltage measurements for the prepared structure were performed according to the same procedures as described in Clause A.3, except that the modulation frequency and voltage for the measurements were 10 Hz and 50 mVrms, respectively.

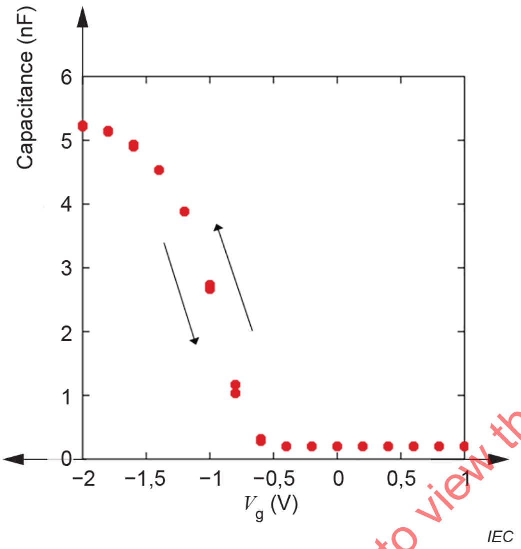
The measured capacitance-voltage curves are plotted in Figure A.5. The arrows in Figure A.5 indicate the bias-sweep direction. The accumulation and depletion of the majority carrier (hole) were clearly observed in the lower voltage range from −1 V to 2 V, accompanied by a considerable reduction of hysteresis in the C-V curves. The hole concentration of the pentacene thin film was evaluated by using Formula (A.1) with the following parameters: A = 0,785 mm^2, e = 1,602 × 10^{-19} C, ε_0 = 8,854 × 10^{-12} Fm^{-1}, ε_s = 3,0 according to the literature [3]. The dashed lines in Figure A.5c) showed the results of least-square fitting to the plots of $1/C^2 - V_g$ curves. The value of $\left|\partial C_{tot}{}^{-2}/\partial V_g\right|$, which was the mean value of the results measured with the forward and backward bias-sweep, was 6,25 × 10^{19} F^{-2}V^{-1}. Finally, the hole concentration was calculated to be 1,2 × 10^{16} cm^{-3}.

The hole concentration of 1,2 × 10^{16} cm^{-3} for pentacene is a plausible value since the carrier concentrations in the order of 10^{15} cm^{-3} to 10^{16} cm^{-3} have been reported for many undoped organic semiconductor thin films [9], [10], [11]. This result confirms that the appropriate design and fabrication of the organic MIS structure are indispensable for evaluating carrier concentrations by using C-V measurements with higher reliability.

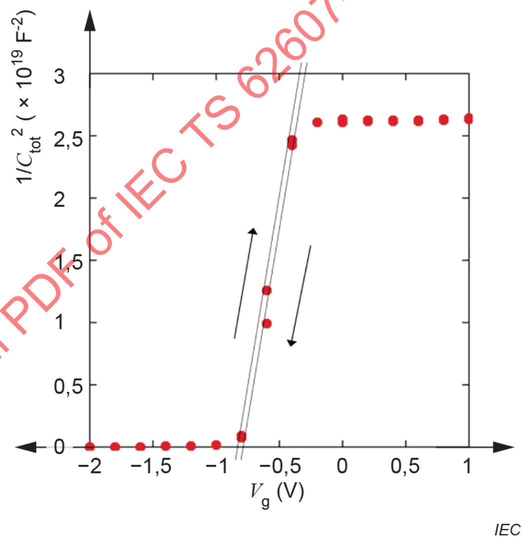
The modulation frequency dependences of the C-V curves measured for the pentacene MIS structure are shown in Figure A.5. As the frequency increases, the accumulated holes at the semiconductor/insulator interface cannot follow the modulation signal. The transition from depletion to accumulation could not be distinguished any longer at modulation frequencies higher than 1 kHz、probably due to the relatively low mobility of the pentacene thin film. Taking into account these frequency responses in the C-V curves, the modulation frequency lower than 1 kHz may be favourable for evaluating the carrier density over a wide range.



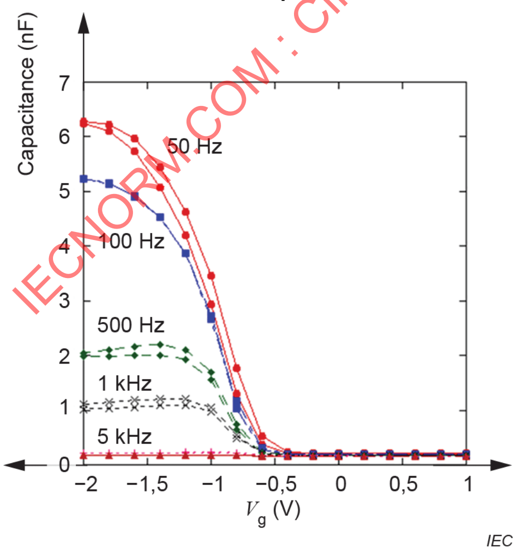
a) A pentacene MIS structure with an ultrathin SAM-coated AlOx insulator



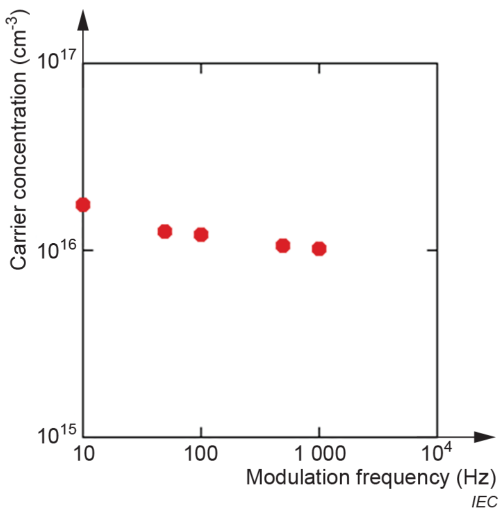
b) Capacitance(C_{tot})-voltage(V_g) curve obtained for this sample



c) C_{tot}^{-2}-V_g plot calculated from the data shown in b)



d) Frequency dependence of capacitance (C_{tot})-voltage (V_g) curve obtained for this sample



e) Frequency dependence of carrier concentration obtained for this sample

Figure A.5 – Capacitance-voltage curves obtained for a pentacene MIS structure with an ultrathin SAM-modified AlOx insulator

A.5 Procedure of Hall-effect measurement

The electrical resistivity of a film specimen obtained with the van der Pauw method is given as follows [10], [11], [12]:

$$\rho = \frac{\pi d}{\ln 2} \frac{R_{\mathrm{AB,CD}} + R_{\mathrm{BC,DA}}}{2} f\left(\frac{R_{\mathrm{AB,CD}}}{R_{\mathrm{BC,DA}}}\right)$$

$$R_{\mathrm{AB,CD}} = \frac{V_{\mathrm{DC}}}{I_{\mathrm{AB}}}, R_{\mathrm{BC,DA}} = \frac{V_{\mathrm{AD}}}{I_{\mathrm{BC}}} \quad \text{(A.2)}$$

where $R_{\mathrm{AB,CD}}$, $R_{\mathrm{BC,DA}}$ are defined as resistances between individual contact points without any magnetic field, and d is the thickness of the organic semiconductor film to be measured. f is a function which follows the relation,

$$\frac{R_{\mathrm{AB,CD}} - R_{\mathrm{BC,DA}}}{R_{\mathrm{AB,CD}} + R_{\mathrm{BC,DA}}} = \frac{f}{\ln 2} \mathrm{arccosh}\left(\frac{1}{2}\exp\left(\frac{\ln 2}{f}\right)\right) \quad \text{(A.3)}$$

The Hall-effect measurement becomes feasible by applying an external magnetic field perpendicular to the film surface [11], [12], [13]. Here, the positive direction of the applied magnetic field is defined as the direction from the top to the bottom side of the specimen. In accordance with Figure 2, V_{CA} and I_{BD} are defined as the potential difference between C and A points, and the electric current flowing from B to D points, respectively. The Hall voltage ($V_{\mathrm{H\text{-}CA}}$) can be obtained as the difference in the V_{CA} values with and without external magnetic fields, and the type of majority carrier in the film (p-type or n-type) can be judged from the sign of $V_{\mathrm{H\text{-}CA}}$. In reality, the measurement of $V_{\mathrm{H\text{-}CA}}$ was repeated for the two opposite directions of the magnetic field and the current flow in order to remove extrinsic components due to undesirable thermoelectric and magnetoresistance effects from the observed potentials. Then, the mean value of the Hall voltage between contacts C and A was calculated as

$$\overline{V}_{\mathrm{H\text{-}CA}} = \frac{V_{\mathrm{H\text{-}CA}}(B_+, I_+) - V_{\mathrm{H\text{-}CA}}(B_-, I_+) + V_{\mathrm{H\text{-}CA}}(B_+, I_-) - V_{\mathrm{H\text{-}CA}}(B_-, I_-)}{4}, \quad \text{(A.4)}$$

where $B_\pm$ and $I_\pm$ indicate the different polarities of the magnetic field and the current flow. In addition, the mean Hall voltage between contacts B and D ($\overline{V}_{\mathrm{H\text{-}BD}}$) under the DC current flow between contacts A and C (I_{AC}) was also measured with the same procedure described above. Finally, the net Hall resistance (ΔR_{H}) was obtained by

$$\Delta R_{\mathrm{H}} = \frac{\overline{V}_{\mathrm{H\text{-}CA}} + \overline{V}_{\mathrm{H\text{-}BD}}}{2I_+}. \quad \text{(A.5)}$$

Here, if we assume that the effective mass transport model based on long-range orders is held for the specimens, the carrier concentration and mobility can be estimated by the following formulas:

$$N = \frac{B}{ed\,\Delta R_{\mathrm{H}}}, \quad \mu = \frac{d}{B}\frac{\Delta R_{\mathrm{H}}}{\rho}, \quad \text{(A.6)}$$