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Letter

On the validity of unintentional doping densities extracted using Mott–Schottky analysis for thin film organic devices

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ABSTRACT

The organic electronic devices are often understood invoking the concept of 'unintentional doping'. However, the applicability and usefulness of this controversial concept is not very clear and is under much recent debate. In this work, we revaluate the validity of this concept through careful experiments and detailed numerical simulations. Specifically, we use the Capacitance Voltage (*CV*) measurement of pentacene devices as a testbed to unravel the role of injecting electrodes and unintentional doping (if any). Indeed, our results indicate that the *CV* of pentacene capacitors can be solely understood in terms of properties of the contact electrodes. The unintentional doping, if present, has an inconsequential role in device performance. Our conclusions indicate that, often, an incorrect interpretation of *CV* results would lead to unphysical values of unintentional doping and have obvious implications towards the fundamental understanding of organic semiconductor device physics, modeling, and characterization; thus resolving many ambiguities in literature by providing a consistent interpretation through a coherent conceptual framework.

1. Introduction

The field of organic electronics has witnessed remarkable technological advancement in recent years; however, the corresponding conceptual understanding is lagging in many aspects. One such controversial idea is related to the depletion region formation in organic semiconductors (OSC) due to unintentional doping [1,2]. Although, both Capacitance Voltage (*CV*) and/or two probe (or 4 probe) resistivity measurements (or current–voltage, *I–V*, measurements) can be used to study the effect of doping in semiconductors, *I-V* measurements are influenced by both carrier density and mobility, and an increase in either of the parameters will result in an increase of current. On the other hand, *CV* measurements are more sensitive to carrier density alone and the associated Mott–Schottky (MS) analysis [3,4] exploits the linearity in $1/C^2 - V$ curves to extract parameters like doping density (N_A), built-in voltage (V_{bi}), and depletion width (W) for OSC, using Eqs. (1) and (2). Here V_A is the applied voltage, ε_s is semiconductor permittivity, A is the area and q is the electronic charge.

$$\frac{\partial 1/C^2}{\partial V} = \frac{2}{\varepsilon_s q N_A A^2} \tag{1}$$

$$W = \sqrt{\frac{2\varepsilon_s (V_{bi} - V_A)}{qN_A}} \tag{2}$$

Traditionally, *CV* is a well-established technique for measuring doping density in inorganic semiconductors [5] and later it was adopted for organic semiconductors [4]. However, the origin of dopants in organic materials is complex and the values of doping densities extracted from

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MS analysis and reported in literature vary drastically. For example, in one study the dopant density is reported to be insignificant [6] whereas, it is used to account for the various observed results in other reports [1,7]. In the absence of any intentional doping [8,9], the linearity in $1/C^2 - V$ behavior is explained by assuming organic semiconductors as being 'unintentionally' doped [1,4,6,10] (which is often misinterpreted as the mobile carrier concentration [11]). However, the sources of such doping are not well established. While oxygen and light are often reported to be critical factors [10,12], surprisingly, unintentional doping was reported even for devices fabricated inside a glove box with inert ambience [3,6,7,13]. The values of unintentional doping density reported vary from 10^{14} to 10^{18} cm^{-3} depending on the thickness of the OSC used [6,10]. While the lower values are apparently insignificant, higher values are a matter of concern as it influences the formation of the depletion region inside the OSC. Accordingly, large variation in depletion thickness, from a few nanometers [14,15] to full thickness of the OSC [6,13] is also reported. Indeed, the reported unintentional doping densities indicate strong device dimension dependence [6,10] – a puzzle that cannot be explained using the traditional MS analysis. Amidst these debates, Kim et al. [6] have shown that depletion capacitance in pentacene does not have voltage dependence even for thick films (1 μm thickness). In another interesting work, Kirchartz et al. [16] has raised doubts about the sensitivity of Mott–Schottky analysis for thin film organic diodes. However, due to lack of an alternative explanation for the Mott–Schottky behavior (apparent linearity in $1/C^2 - V$ plot), the unintentional doping concept is continuously used to explain and quantify the physics of organic devices. At the same time, the critical role of contacts on capacitance measurements is not well understood. Although there have been some related reports [17], quantitative studies on this aspect are still lacking, especially for thin film organic devices.

In this work we critically analyze the idea of unintentional doping and depletion region formation in thin film organic devices. For this, we investigate pentacene Metal–Insulator–Semiconductor (MIS) capacitors through experiments and simulations. Specifically, we show for the first time that (i) the *CV* characteristics can be entirely explained in terms of injected carriers from the contact electrode, without invoking the concept of any "unintentional dopants", (ii) if not carefully considered, MS analysis can lead to an incorrect interpretation of *CV* curves and the organic semiconductor can easily be misinterpreted as being unintentionally doped, and (iii) our results resolve the device dimension dependence of unintentional doping densities reported in literature [6,18–22]. The manuscript is arranged as follows: Section 2 describes experimental details. Experimental data, simulation results and their implication on OSC physics are discussed in Section 3.

2. Experimental details

A p-type highly doped silicon wafer of resistivity 0.001–0.002 ohm-cm was used as the substrate. 66 nm of high quality oxide was thermally grown on it. Back side oxide was etched and aluminum was deposited as the substrate contact metal (bottom contact, see inset of Fig. 1). Pentacene, triple sublimed with 99.9% purity from Sigma Aldrich, was evaporated using a shadow mask with deposition rate of 0.2 nm/s. 62 nm thickness of the pentacene was confirmed using Ambios profilometer. Gold contacts were evaporated on top of pentacene using the shadow mask with an effective device area of 1.3×10^{-3} cm^2. Keithely 4200 semiconductor characterization system was used for device characterization. The voltage was applied at the bottom electrode while the top contact was connected to the ground. Note that the entire device fabrication and characterization was conducted in an ambient atmosphere with a humidity of 55% and at room temperature. The results presented in this work represent a typical dataset measured over multiple samples in different runs.

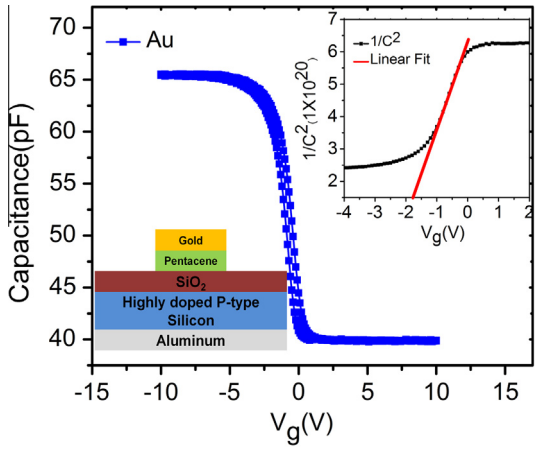

Fig. 1. Capacitance voltage characteristics for pentacene capacitors with gold contacts measured at 10 kHz. Bottom inset shows the pentacene MISM capacitor schematic. Top inset shows the Mott–Schottky analysis to extract N_A and V_{bi}.

3. Results and discussion

Fig. 1 shows the measured *CV* characteristics. The measurement frequency was 10 kHz and negligible hysteresis was observed. The capacitance shows an apparent transition from accumulation to depletion. The capacitance at negative biases (C_{max}) saturates to a value close to oxide capacitance (C_{ox}) given by Eq. (3), while for positive biases, it reaches a constant value of C_{min}, equivalent to series capacitance of oxide and pentacene ($C_{pentacene}$), given by Eq. (4).

$$C_{max} = C_{ox} = \frac{\varepsilon_{ox} A}{t_{ox}} \tag{3}$$

$$C_{min} = \frac{C_{ox} \times C_{pentacene}}{C_{ox} + C_{pentacene}}, \tag{4}$$

where t_{ox} is oxide thickness and ε_{ox} is dielectric constant of the oxide. The dielectric constant of pentacene was found to be 5 (back extracted from C_{min}, see Eq. (4)). Although,