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Study on the basic capacitance–voltage characteristics of organic molecular semiconductors

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A B S T R A C T

Capacitance–voltage (*C–V*) characteristics of organic molecular semiconductors attracted much research interest recently, but no convincing physical mechanism has been established so far. In this work, the *C–V* characteristics of pentacene-based devices have been systematically investigated at various frequencies. Only one peak occurs when the measuring frequency is less than 3 kHz or greater than 8 kHz. While within the frequency range between the two, two *C–V* peaks are observed with quite different dependence on temperature, which suggests that the origins of these two *C–V* peaks are respectively mobile holes and trapped carriers. This conclusion is also experimentally validated with the *C–V* characteristics of intentionally doped devices.

1. Introduction

Capacitance-based steady-state methods have attracted much attention since the capacitance–voltage (*C–V*) characteristics of organic semiconductors were shown to vary sensitively with any change of the carrier transport [1–11] in past several years. However, the corresponding conceptual understanding is still lagging. It has been commonly observed that only one peak appears in the *C–V* characteristics when the polarity of the bias applied across the organic semiconductor is changed from reverse to forward [1–9]. The origin of such a peak was often assumed as the effect of depletion layer capacitance since the C^{-2} vs V plots of some organic devices were found approximately linear in a narrow voltage range. But it is now recognized that such an assumption is invalid due to the totally different relationship between applied voltage and space charge width in organic devices [12,13]. Lately Tripathi and Mohapatra proposed the model of diffusion limited capacitance [1]. They studied the capacitance of space charge limited organic diodes and found that all the $C^{-2/3}$ vs V plots were close to linear in their experiment. The effect of energy level disorder on the device capacitance has also been studied and simulated with the extended Gaussian disorder model [14]. Besides, the majority carrier injection [15] or the minority carrier injection [5] was considered responsible for this *C–V* peak as well. More recently, however, Akanksha Sharma et al. observed the appearance of two peaks in *C–V* characteristics of copper phthalocyanine (CuPc) based devices [11]. Their results provided more experimental evidence for capacitance-related behaviors but also caused more difficulties in analyzing the basic *C–V* characteristics of organic molecular semiconductors. So far, there has not been established a convincing physical mechanism for the measured *C–V* characteristics. It is even not clear how many peaks may exist in the *C–V* characteristics of organic devices.

It is worth noticing that almost all of the studies on *C–V* characteristics were carried out at room temperature with a single measuring frequency, which makes it difficult to distinguish different capacitance-related factors. In this work, the *C–V* characteristics of the device ITO/pentacene (250 nm)/Au are measured systematically at various frequencies and temperatures. Two kinds of *C–V* peaks are observed with quite different dependence on temperature. The origins of these two different *C–V* peaks are experimentally proved to be the mobile holes and trapped carriers respectively.

2. Experimental details

The devices were fabricated on indium-tin oxide (ITO)-coated glass substrates with sheet resistance about 17 Ω/sq. All the materials used in the present experiment are commercially available. The organic devices were thermally deposited in ultra-high vacuum system with base pressure 2×10^{-6} Pa. The area of the organic device was 9 mm^2, defined by 3-mm-wide ITO stripes over crossed by 3-mm-wide top metal straps. The current–voltage (*I–V*) and *C–V* measurements were recorded with Keithley 236 and HP 4284A LCR METER. Parallel model was chosen to measure

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capacitance characteristics with frequency-varied AC modulation signals. All the measurements were carried out in a liquid nitrogen Dewar bottle (less than 1 Pa) in dark with a temperature controller, which could adjust the temperature from 78 to 300 K continuously. Forward bias is defined as a positive potential applied to the ITO anode with respect to the Au cathode.

3. Results and discussion

In order to avoid the disruption caused by minority carrier, hole-only device ITO/pentacene (250 nm)/Au was fabricated for this study. Pentacene is an excellent hole transport material with ionization potential 4.9 eV [16]. The measured *C–V* (at 1 kHz) and *I–V* characteristics of this device are shown in Fig. 1. The current of this device is higher than 6 mA at 2.5 V. On the contrary, the current at reverse bias is less than 10^{-2} mA. Such an *I–V* curve implies that the hole injection at pentacene/Au interface is less efficient than that at ITO/pentacene interface, even though the work function of Au is higher. It was reported recently that thermally deposited Au would induce an extra barrier at pentacene/Au interface [17]. This barrier will reduce the actual work function of the Au layer, resulting in lower current at reverse bias. At −3 V, the value of capacitance is 1.76 nF. This value keeps almost unchanged from −3 V to −1 V and then increases slowly to 1.88 nF at 0 V. At forward bias, the capacitance increases sharply with bias, and a peak occurs at 1.1 V with a value of 4.87 nF; after that, the capacitance decreases to 3.64 nF at 2.7 V.

The frequency-dependence of the *C–V* characteristics at room temperature (295 K) is shown in Fig. 2. The measuring frequency changes from 2 kHz to 10 kHz. The shape of the *C–V* curve measured at 2 kHz is almost the same as that measured at 1 kHz, except that the peak value decreases to 3.32 nF. At 3 kHz, a distinct peak is observed at 1 V with a value of 2.73 nF while a shoulder appears at 0.27 V. At 5 kHz, two separated peaks are clearly observed. The first peak appears at 0.27 V with a value of 2.11 nF and the second peak appears at 0.85 V with a value of 2.18 nF. At 8 kHz, the peak at 0.27 V remains with a value of 2.04 nF, but the second peak is no longer discernible clearly. Raising the measuring frequency to 10 kHz results in further weakening of the second peak: at this frequency, only one peak exists at 0.27 V, with a value of 2.01 nF followed by a monotonously decreasing tail.

To provide further insight into the origins of these two peaks, temperature-varied *C–V* characteristics were measured at 5 kHz and the results are shown in Fig. 3 (a), where the inset shows its *I–V* characteristics at different temperatures. The close-up of the first peak is shown in Fig. 3 (b). It shows clearly that, as the temperature decreases, the intensity of peak one decreases

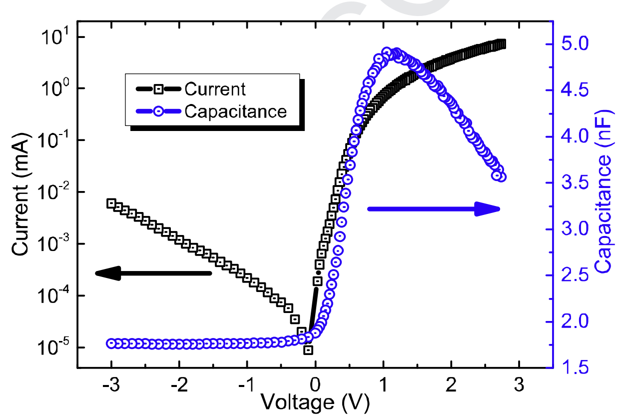

Fig. 1. The *C–V* (1 kHz) and *I–V* characteristics of the device ITO/pentacene (250 nm)/Au at 295 K.

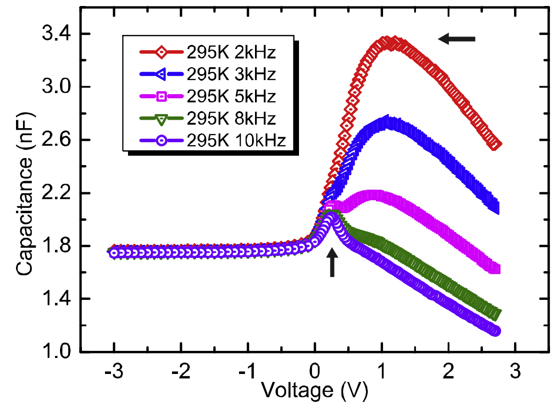

Fig. 2. The *C–V* characteristics of the device ITO/pentacene (250 nm)/Au measured with different frequencies at 295 K.

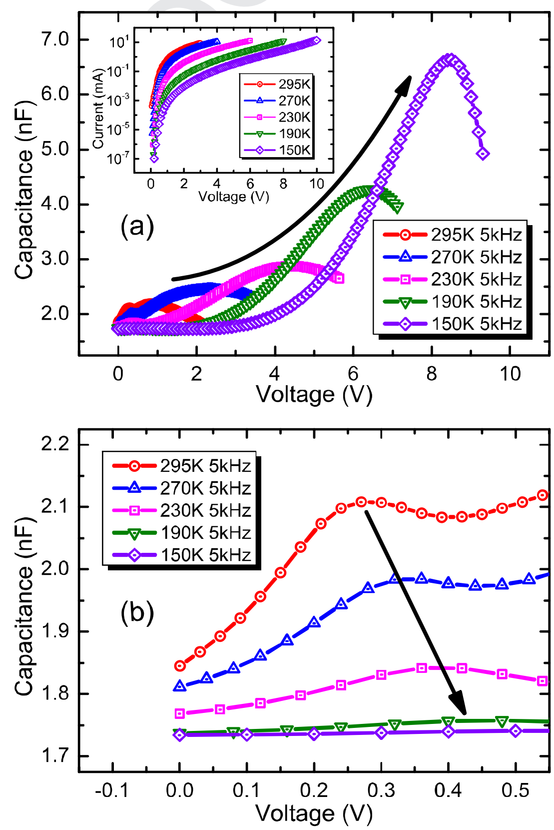

Fig. 3. The *C–V* characteristics of the device ITO/pentacene (250 nm)/Au measured at different temperatures with the measuring frequency 5 kHz. Inset in (a) is the *I–V* characteristics of the same device measured at different temperatures. (b) Is the close-up of the first peak. The arrows show the shift of the two peaks as the temperature decreases.

whereas that of peak two increases; the location of the first peak shows a tiny shift to higher bias (less than 0.15 V) while shift of the second peak is pretty obvious. At room temperature, the first peak appears at 0.27 V with a value of 2.11 nF, but this peak almost disappears at 150 K. Meanwhile, the value of peak two increases from 2.18 nF to 6.63 nF and its location shifts from 0.85 V to 8.5 V.

Evidently, two different kinds of *C–V* peaks exist in the *C–V* characteristics of this device. The first peak occurs when the injection is tiny. In order to completely eliminate the interference from external carriers (diffusion [2] or injection [5,15]), the *C–V* characteristic of the device ITO/LiF (75 nm)/pentacene

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