Large apparent inductance in organic Schottky diodes at low frequency

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A large low frequency inductance is found in a Schottky diode composed of regioregular poly(3-hexylthiophene) and aluminum. This apparent inductance is evident in response to both swept frequency sinusoidal, ramp and step voltage inputs above a threshold voltage. The constant slope of the current in response to a voltage step suggests an incredibly large inductance (a few hundred megahenry) in a device that is only 2000 μm^3 in size. A number of potential mechanisms including chemical reactions, barrier modulation, and memory effects are evaluated in order to find a suitable explanation for the inductive behavior. Similarity in the dc characteristics of the organic Schottky diode and organic bistable devices that are being applied as memory suggests that the current leads the voltage due to increments in tunneling current that occur as charges are gradually stored in localized states. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2189208]

I. INTRODUCTION

Most crystalline integrated circuits consist of combinations of resistors, capacitors, diodes, and transistors. Although inductance is necessary for many analog circuits, especially radio frequency (rf) circuits, the lack of inductors with reasonable values and small size has forced chip designers to use simulated inductor circuits typically composed of a few amplifiers to mimic inductor characteristics.[1] Replacement of an inductor with a number of transistors is not a serious issue in silicon technology since the final circuit cost and size are much less than that of a real inductor. In organic electronic circuits transistors usually occupy much more space than the crystalline transistors because of the high channel width required to increase the gain of each transistor and reduce the stray current that are found to arise at device edges.[2] Therefore the inclusion of extra transistors can increase the size of a chip significantly in an organic integrated circuit.

In this paper a low frequency inductivelike behavior in an organic Schottky diode is presented that potentially can be used in electronic circuits such as filters and oscillators. Mechanisms are discussed to suggest an explanation for the apparent inductive characteristic.

II. BACKGROUND

In general when a semiconductor makes contact with a metal, band bending occurs in the semiconductor close to the metal/semiconductor interface. The contact is a Schottky contact if this band bending produces a barrier for the majority carriers in the semiconductor. When an external voltage is applied, the barrier results in the rectification property that is used to make Schottky diodes. The dc behavior of a Schottky diode is generally described by the diffusion-thermionic model that predicts an exponential relationship between current density (J) and applied voltage (V),[3]

$$J = J_0 \exp\left(-\frac{q\varphi_b}{kT}\right)\left[\exp\left(\frac{qV}{nkT}\right) - 1\right], \tag{1}$$

where q is the unit charge, $q\varphi_b$ is the barrier height, k is the Boltzman constant, T is the absolute temperature, n is an empirical constant called the ideality factor, and J_0 is the saturation current density.

The current in the diffusion-thermionic theory is only based on the number of carriers that have enough energy to pass over the barrier, whereas a portion of the total current is from the carriers that have tunneled through the barrier. This type of current is called field emission current and it is usually so small in the forward bias that it is either ignored or is absorbed in the ideality factor n.[3] However, the effect of tunneling current can be considerable if the doping level is high enough to produce a narrow barrier[3] or when the density of localized states close to the metal-semiconductor interface is very high.[4]

Organic semiconductors exhibit an enormous density of localized states at their surfaces due to their noncrystalline structure and impurities. These localized states are usually modeled as traps [5] and the relaxation time associated with them is represented by a series resistor-capacitor (RC) circuit in the ac model.[6] The time constant for traps ($\tau_t = R_t C_t$) typically varies from a few nanoseconds for fast traps to a few minutes for slow traps depending on the energy level of traps in the semiconductor.[7] Usually deep traps have larger time constants (τ_t) than shallow traps.

The depletion region, resulting from the band bending at the metal-semiconductor interface, also behaves like a capacitor (C_d) and a parallel resistor (R_d) in response to small signals. The small signal equivalent circuit for an organic Schottky diode is shown in Fig. 1, where the bulk semiconductor region is modeled with another parallel RC (R_b and C_b) circuit and the effect of contact resistance is represented by a series resistor (R_s).[8]

Since the ac model is applicable at a specific dc bias, the device might show different trap time constants (τ_t) at dif-

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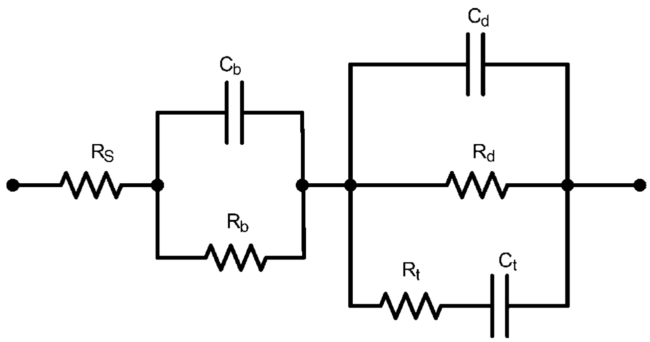

FIG. 1. ac model of an organic Schottky diode consisting of bulk capacitance and resistance (C_b-R_b), junction capacitance and resistance (C_d-R_d), trap associated capacitance and resistance (C_t-R_t) and the bulk semiconductor resistance R_S.

ferent biases. That is because of the change in the Fermi level in the semiconductor that might reach the energy level of deep or shallow traps.[9] Although the ac model shown in Fig. 1 can explain the electrical properties of our device at low voltages and high frequencies, above a threshold voltage and at low frequencies inductive behavior is observed that cannot be described with this standard model.

III. EXPERIMENTS

Regioregular poly(3-hexylthiophene) (rr-P3HT), a well characterized and relatively stable P-type organic semiconductor,[10] is chosen as the semiconductor with which to build an organic Schottky diode. To construct a Schottky diode a thin film of the semiconductor is sandwiched between a low work function metal (aluminum, WF=4.3 eV) and a high work function metal (gold, WF=5.1 eV). Generation of a Schottky contact between rr-P3HT and aluminum has been demonstrated previously.[11] The gold/organic contact produces a small barrier[12] which is negligible compared to the barrier at the aluminum contact. Therefore the gold contact works as the anode and the aluminum as the cathode of the diode.

Figure 2 shows the cross section of the device. The first step is to pattern a 45 nm thick gold microelectrode on a Si/SiO_2 substrate using photolithography. A solution of 0.8% (weight) of rr-P3HT, supplied by ADS,[13] in chloroform is used to make an 80 nm thick polymer layer by dipping the gold electrode into the solution and pulling it out slowly. Then the sample is held at 100 °C in an oven for 55 min to evaporate any residual solvent and anneal the semiconductor film.[14]

The entire process is done in air in a class 1000 cleanroom. Oxygen and moisture have a destructive effect on the semiconducting properties of most organic semiconductors.[15,16] They act as dopants in the organic semiconductors and the doping level is not reproducible in an exposed semiconductor film.[17] To reduce the doping level the sample is then placed in the chamber of an evaporator with a vacuum of 2×10^{-7} torr for 18 h.[18] Tape (3M Scotch) is applied before insertion into the chamber as a passive layer to mask the gold electrode during aluminum deposition which makes the effective area of the gold electrode 5 mm $\times 4$ μm. A 500 nm thick aluminum layer is then deposited on the sample by e-beam evaporation. The wide and thick layer of aluminum is intended to encapsulate the organic material.[19]

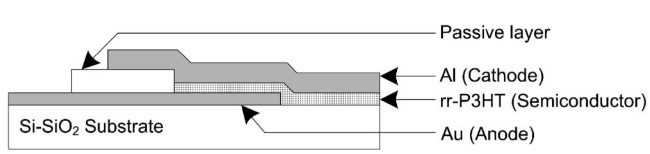

FIG. 2. The side view of the organic Schottky diode made of rr-P3HT (not to scale).

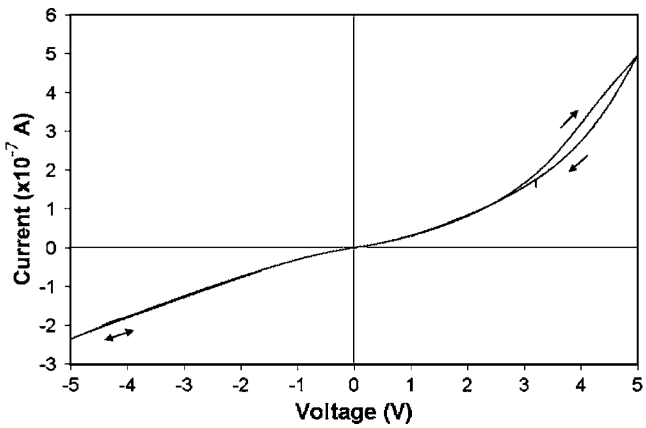

FIG. 3. Current-voltage (I-V) characteristic of the organic Schottky diode in the range of ±5 V showing a capacitive hysteresis loop.

To study the dc and ac characteristics of the device more than ten devices were fabricated and tested, all showing similar electrical characteristics. In this report the results of measurements from one of the samples are presented. The electrical characteristics of samples are measured with a Solartron SI1287 electrochemical interface and a Solartron SI1260 impedance analyzer. All measurements are done in air in the absence of light.

IV. RESULTS

To determine the dc characteristics of the device a triangular voltage starting from 0 V and increasing at a rate of 50 mV/s is applied and the current is recorded. When the amplitude is limited to ±5 V, the forward current is only two times higher than the reverse current (Fig. 3). In contrast with crystalline Schottky diodes that show a very sharp rise in the forward current, the bulk resistance of organic semiconductors[20] and the space charge effect[21] make the slope of the forward current small in organic Schottky diodes. Also the reverse current saturates in crystalline Schottky diodes, whereas in this nonuniform Schottky contact parallel resistive paths appear that make the reverse current linearly dependent on the voltage.[22] As has been described previously reduction of these parallel paths can increase the rectification ratio to values as high as 100. This is achieved by application of high voltages which burn resistive paths.[22] Since this process might change the electrical and physical properties of the semiconductor close to the damaged regions, no attempt is made to increase the rectification ratio in the experiments described in this paper.

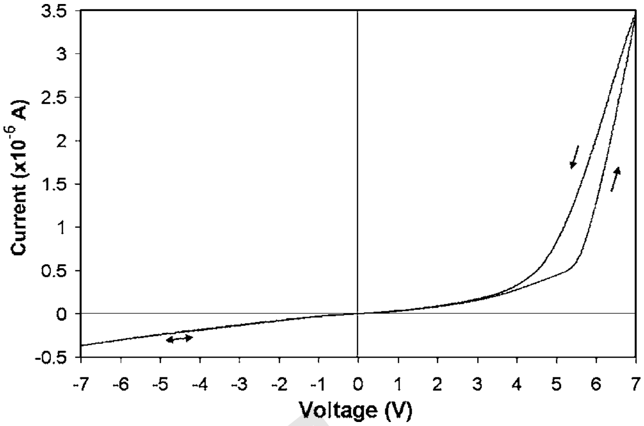

FIG. 4. Current-voltage (I-V) characteristic of the organic Schottky diode in the range of ±7 V showing an inductive hysteresis loop.

The most distinctive effect in Fig. 3 is the lag of the current when the voltage is scanned down from 5 to 0 V. According to the ac model, represented in Fig. 1, capacitive properties of the device produce such a loop that disappears when the speed of the scan voltage is reduced.

Increasing the amplitude of the scan voltage to 7 V shows a very different current-voltage (I-V) curve (Fig. 4). Although the reverse current maintains its resistive property, a sharp slope appears at voltages larger than a threshold (V_{th}=5.4 V) when the voltage is scanned from 0 to 7 V. Also the current shows an inductive hysteresis loop that is not predicted by the ac model in Fig. 1. Scanning voltage in different ranges has shown that the inductive loop appears when the voltage is more than the threshold and it is not necessary to scan voltage both in forward and reverse biases.

To study the ac characteristic of the organic Schottky diode the impedance of the device is measured at a number of biases. Figure 5 shows the magnitude and phase of impedance at 4 V dc bias after the dc voltage is scanned from 0 to 4 V. The amplitude of the modulated ac voltage is set at 0.2 V. The plot shows a pole at 10 Hz that suggests a capacitance of 2 nF and a resistance of 7 MΩ $[f=(2\pi RC)^{-1}]$. Since the capacitance of the junction is expected to be close to 2 nF due to the dimensions of the junction, the observed pole is likely due to the junction property (C_j and R_j). The ac model introduced in Fig. 1 predicts two more poles for the impedance that are expected to be beyond of the measured frequency range.

The bode plot of the impedance at 7 V bias is represented in Fig. 6. The shift of the junction pole $[f=(2\pi R_j C_j)^{-1}]$ from 10 Hz to the higher frequency is expected due to the reduction of R_j above the threshold voltage in Fig. 4. The positive phase of the impedance at frequencies below 10 Hz is a sign of the apparent inductance which can be modeled as a parallel inductor. An estimated value of 5 MH for the inductor is estimated by considering the 3 dB drop in the magnitude at 0.02 Hz (see arrow) as a new pole with a zero at 0 Hz. However, the absence of the expected phase (45°) at the proposed pole suggests a more complicated model, which is not considered in this paper.

Since the inductive behavior of the junction appears at very low frequencies, the characteristic can be studied by

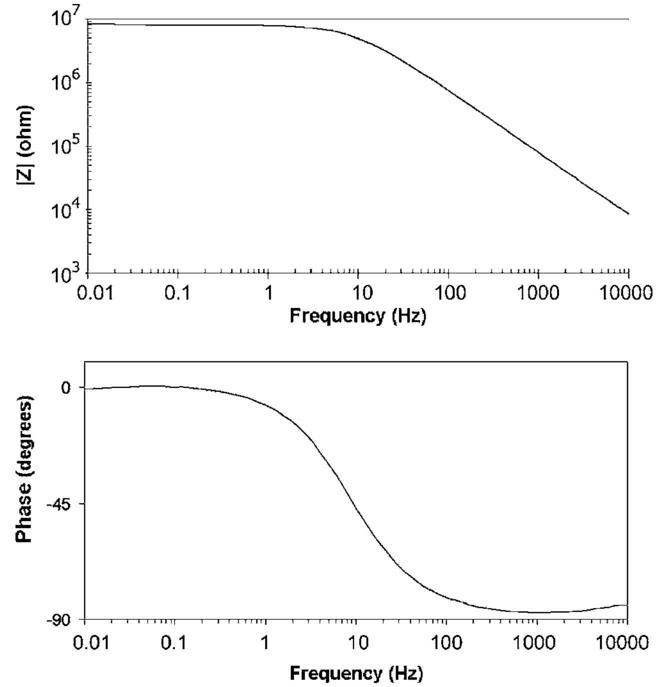

FIG. 5. The magnitude and phase of small signal impedance of the organic Schottky diode at 4 V dc bias.

application of pulses to the diode. Figure 7 shows the measured current in response to the applied pulses. When a 5 V pulse is applied from 0 V bias the current settles very quickly to 4.25×10^{-7} A, while the application of 7 V shows a gradual increase in the current that confirms inductive property of the junction at large bias. According to the basic inductor equation ($V=L\Delta I/\Delta t$), the apparent inductance (L) is calculated as 860 MH from the slope of the current ($\Delta I/\Delta t$).

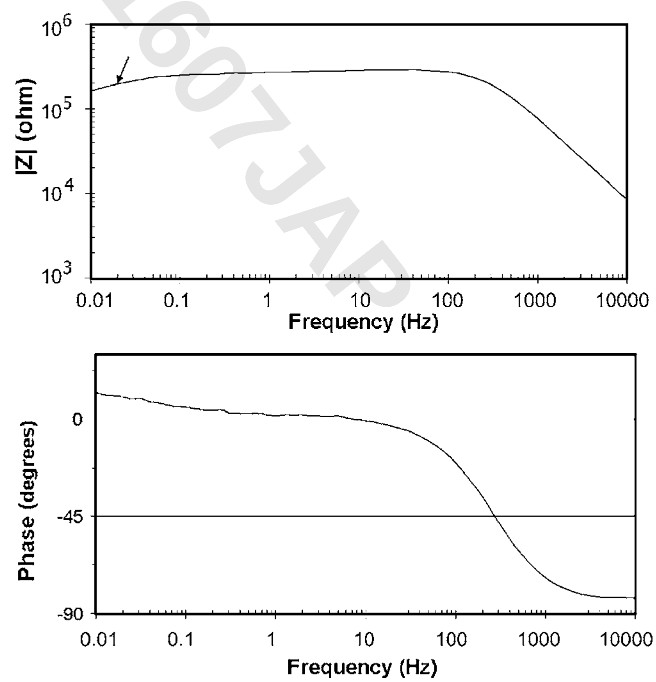

FIG. 6. The magnitude and phase of small signal impedance of the organic Schottky diode at 7 V dc bias.

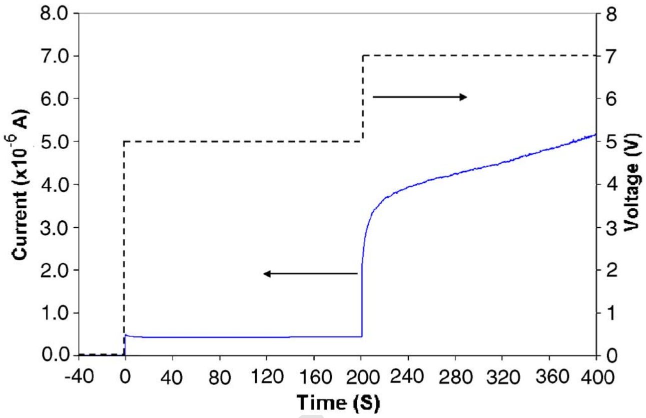

FIG. 7. The organic Schottky diode current in response to a voltage pulse.

An attempt to keep the device at 7 V bias for long enough to observe saturation failed due to a sudden drop of the current perhaps because of joule heating.[23]

V. DISCUSSION

Inductivelike behavior is observed in response to step, ramp, and swept sine inputs. In this section we evaluate a number of potential mechanisms to find an explanation for the apparent inductive characteristics.

Almost all electronic devices show inductive properties at high frequencies due to their connection leads,[24] but the inductance magnitude seldom reaches the microhenry range, whereas a large low frequency inductance is observed in this case in a relatively small device.

Chemical reactions and changing oxidation states in the organic layer are unlikely mechanisms because the current generally does not increase with time in response to a constant applied voltage in electrochemical reactions.[25]

The barrier height reduction [$q\varphi_b$ in Eq. (1)] that results from the image force effect[3] when dopants move slowly toward the junction is very unlikely to lead to the current increase in Fig. 7. Indeed the barrier is expected to increase in the forward bias[3] rather than decrease which would lead to a drop of current with time, as opposed to the observed increase.

The change in current (Fig. 7) resembles the drift of electrical characteristics that is commonly observed in metal-oxide semiconductor (MOS) devices, which is mostly due to the ion motion. Although in organic Schottky diode accumulation of ions at the metal-semiconductor interface in response to dc applied field produces more localized states that can potentially increase the tunneling current, to obtain the positive phase in the impedance test (Fig. 6) ions have to be accumulated and evacuated from the interface in response to the ac signal. In the impedance test a large dc bias voltage (7 V) and a small ac signal (200 mV) are simultaneously applied, with the large dc bias maintaining the electric field in one direction. In such a unidirectional field the accumulated ions are not expected to leave the surface in response to a minor ac perturbation in the applied field. The effect of the surface charge should appear only as a continual[26] shift in the voltage response which cannot explain the observed ac response of the Schottky diode.

As another possibility, metal ions diffused from one of the electrodes might be spread throughout the organic layer in response to the applied electric field. Such a mechanism might lead to an increase in the conductivity of the semiconductor and result in a large change in the current similar to that in the organic flash memory proposed by Ma *et al.*[27] Although diffusion of aluminum ions from the top electrode into the organic semiconductor is very probable,[28] the field in the forward bias is expected to pull these Al^{3+} ions back towards the aluminum electrode, reducing the spreading and leading to a drop in current instead of the observed increase. The diffusion of gold ions from the bottom electrode is very unlikely due to the stability of the gold/organic junction.[29]

In summary the effect of mobile ions in the organic layer cannot explain the inductivelike behavior of the Schottky junction.

Organic bistable devices (OBDs) known as organic memory show a response similar to that in Fig. 4, in which current is lower during scan up than it is in the down scan.[30,31] The mechanism of the memory effect in the OBDs is not well understood, but modeling results suggest that it is due to an increase in tunneling current when charges are stored close to the barrier layer.[32] Similarly, storage of charge in the localized states close to the Schottky barrier in our organic Schottky diode could increase the tunneling current at the junction. A high density of localized states in the middle of the band gap at the surface of the semiconductor that can work as deep-slow traps is very common in amorphous semiconductors due to impurities and defects in the organic layer.[6]

Although the gradual increase in current in our device is very different from the sudden change in current in the OBDs, the large time constant associated with the deep traps could explain the difference in the time response. Charging and discharging of the deep-slow traps in the organic Schottky diode could lead to an increase and decrease, respectively, of the tunneling current in the Schottky diode.

Figure 8 shows the band diagram of the junction at different biases that can explain the apparent inductive behavior. In the band diagram donorlike states form deep traps with a Gaussian distribution close to the midgap.[9] At 0 V bias [Fig. 8(a)], when Fermi energy is aligned in the metal and the semiconductor, donorlike states are neutralized. Therefore they cannot affect the electrical characteristics of the device. Similarly the charging of the localized states does not change in the reverse bias [Fig. 8(b)]. In the forward bias the application of a voltage higher than a certain threshold leads the Fermi level to reach donorlike energies [Fig. 8(c)]. In the steady state condition the traps having energies greater than the Fermi level are charged, enhancing the tunneling current in the device, as in OBDs.[31] Since these are slow traps, reaching to the equilibrium is not immediate and as a result the tunneling current increases gradually with time.

The proposed mechanism can explain the ac characteristics of the device. At high frequencies the slow traps cannot follow the charging and discharging processes. Hence the impedance test at high frequencies shows the *RC* property of the device. At low enough frequencies when the bias voltage is above the threshold the slow traps can be charged and

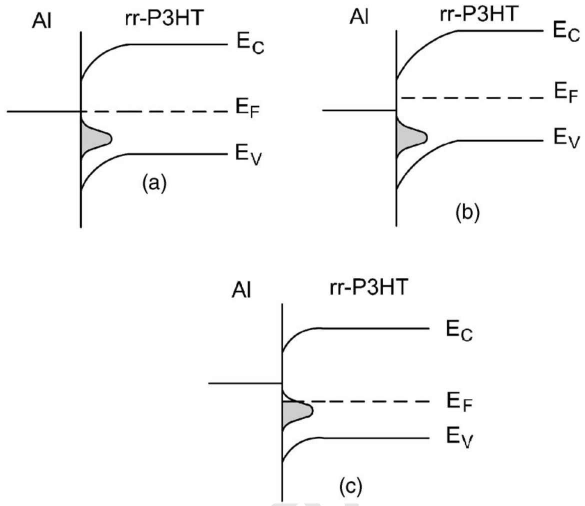

FIG. 8. The proposed band diagram of the Schottky junction between the aluminum and rr-P3HT with a Gaussian distribution of donorlike localized states (a) at equilibrium, (b) the reverse bias, and (c) the forward bias above the threshold. Impurities are neutralized in the (a) and (b), while the localized states located above the Fermi level are ionized in (c).

discharged in response to the applied ac signal. The slope of the current in Fig. 7 suggests time constants for the traps at least on the order of minutes.

The observed apparent inductance might be used to make inductor-capacitor (LC)-type oscillators or low frequency filters for organic integrated circuits. However, for rf applications kilohertz range or higher frequency is desired. Decreasing the charging time constant of traps might shift the apparent inductive behavior to the higher frequencies. Further study on the charging status of the localized states is required for a better understanding of the mechanism that leads to the apparent inductive behavior. Determination of the effective parameters influencing the observed inductance, such as type and quantities of impurities, electrodes composition, and the fabrication process, is necessary to engineer a device for the use in electronic circuits over a wide frequency range and with a controlled inductance value.

VI. CONCLUSION

The dc and ac characteristics of an organic Schottky diode are studied, showing an apparently inductive behavior. Current-voltage characteristics, impedance measurements, and step responses of the device are plotted for voltages below and above the threshold of the inductivelike characteristic. The results of measurements suggest a parallel megahenry range inductor when the bias voltage is higher than a threshold of 5.4 V. Evaluation of numerous possible mechanisms suggests that the inductive behavior is likely due to the increase of tunneling current with increased charging of deep localized states. More study of the organic Schottky diode and the role of localized states are required to extend the frequency range and to tune the inductance values for various applications.

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