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Capacitance of Organic Schottky Diodes Based on Copper Phthalocyanine (CuPc) *

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The capacitance of an organic Schottky diode based on copper phthalocyanine (CuPc) is investigated. Based on the organic small-signal equivalent model established, we calculate the reverse capacitance $C_{\rm Metal}$ *of the organic Schottky diode with different kinds of metal cathodes (Mg, Al, Au). It is found that the reverse capacitance of the organic Schottky diode shows behavior as* $C_{\rm Mg} > C_{\rm Al} > C_{\rm Au}$ *at the same frequency, and according to our analysis, the reverse Schottky junction capacitance* C_j *is expected to have little effect on the reverse capacitance of the organic Schottky diode, and the space-charge limited current capacitance* $C_{\rm S}$ *is considered to dominate the reverse capacitance, which limits the improvement of frequency characteristics of organic Schottky diodes.*

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Considerable efforts have been devoted to the investigation of organic semiconductor devices because of their promising applications in rf identification (RFID) tags,[1−3] active matrix backplanes for flexible displays,[4] and sensor arrays.[5] One of the most important potential applications is organic RFID tags, which are better than silicon RFID tags[3,6] because of their lower cost. The frequency characteristics of organic semiconductor devices, however, still need to be improved compared to inorganic semiconductor devices, which is the main roadblock to the implementation of high-frequency RFID tags based on organic semiconductors.

There are two competing approaches to make organic high-frequency devices. They can be based either on an organic thin-film transistor[7] or on a vertical organic diode which includes organic Schottky diodes[1,8] and p-n junction diodes.[9] In general, for organic Schottky diodes, two methods have been used to improve the frequency characteristics: one is to increase the carrier mobility of the organic material, the other is to decrease the active area of the organic Schottky diode. For example, Ma *et al.*[10] demonstrated a high-performance organic diode based on C_{60} which shows a megahertz frequency response. Researchers reported that Schottky diodes based on pentacene have a higher cut-off frequency compared with the Schottky diodes based on copper phthalocyanine (CuPc) because of pentacene's higher carrier mobility,[11] and a high-frequency organic Schottky diode was also fabricated by Ai *et al.*[12] with an active area of $1.7\times10^{-5}\,{\rm cm}^2$, which could operate at 14 MHz.

As far as we know, reverse Schottky junction capacitance C_j is the main limit for high-frequency characteristics of inorganic Schottky diodes. When an inorganic Schottky diode is working in a high-frequency circuit, the lower reverse Schottky junction capacitance will lead to the higher-frequency characteristics of the diode because of the impedance of the junction capacitance $X_{{\rm C}_j} = 1/2\pi c_j f$ (f: frequency). For organic Schottky diodes, space-charge limited current (SCLC) capacitance $C_{\rm S}$ and Schottky junction capacitance C_j are believed to be the two existing kinds of capacitance;[13−15] however, which capacitance is the main limit for the higher frequency characteristics of organic Schottky diodes is still unclear.

In this study, organic Schottky diodes based on CuPc with the configuration ITO/CuPc(40 nm)/metal cathode(80 nm) are fabricated. According to the established organic Schottky diode small-signal equivalent model with different kinds of metal cathodes (Mg, Al, Au), the capacitance of organic Schottky diodes is investigated, and it is found that reverse capacitance $C_{\rm Metal}$ of organic Schottky diodes with different metal cathodes are as $C_{\rm Mg} > C_{\rm Al} > C_{\rm Au}$ at the same frequency. By theoretical analysis, SCLC capacitance $C_{\rm S}$ instead of C_j is found to dominate the reverse capacitance of organic Schottky diodes, which will be the main roadblock for the implementation of high-frequency organic Schottky diodes based on CuPc.

The organic Schottky diode is built on a glass substrate precoated with indium tin oxide (ITO) film with a configuration of ITO/CuPc(40 nm)/metal

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**To whom correspondence should be addressed. Email: zhaoxinwu@mail.xjtu.edu.cn cathode(80 nm), and three different diodes are fabricated with three metal cathodes (Au, Al, Mg), respectively. The pressure during thermal evaporation for deposition is 1×10^{-3} Pa. CuPc and metal cathode are subsequently deposited at a rate of 0.3 nm/s (the deposition rate of Au is 0.1 nm/s). The active area of the device is 0.12 cm^2.

Figure 1 schematically shows the measuring circuit. The signal generator (RIGOL DG1022) supplies the ac inputs with different frequencies. D is the organic Schottky diode we fabricated. The load resistor $R = 100\,\Omega$. Both the ac inputs and their outputs are measured by an oscilloscope (Tektronix TDS 2024B) at different frequencies. The peak value of input voltages ($V_{\rm in+}$, $V_{\rm in-}$) and output voltages ($V_{\rm out+}$, $V_{\rm out-}$) are all recorded at the same time. All the measurements are carried out at room temperature under ambient conditions.

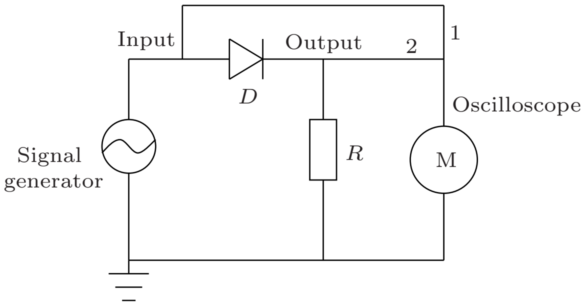

Fig. 1. (a) Measuring circuit diagram for input-output characteristics of CuPc diodes.

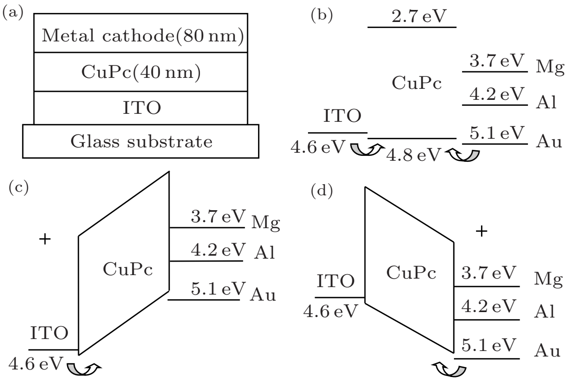

Fig. 2. (a) Schematic diagram of the device structure. (b) Energy level diagram with different metal cathodes (Au, Al, Mg). (c) Energy diagram when diodes are forward-biased. (d) Energy diagram when diodes are reverse-biased.

In order to investigate the capacitance of the organic Schottky diode, we establish its small-signal equivalent model. Figure 2(a) shows the device structure of the organic Schottky diodes we fabricated and Fig. 2(b) shows the energy level diagram with different cathodes. The work functions of ITO, Au, Al and Mg are 4.6 eV, 5.1 eV, 4.2 eV and 3.7 eV respectively. CuPc acts as an electron blocking layer with a low unoccupied molecular orbital (LUMO) level of 2.7 eV. When the organic Schottky diodes are forward-biased (reverse-biased), the great offset between the work function of metal cathodes (ITO) and the LUMO level of CuPc serves to reduce the efficiency of the electron injection and to guarantee the holes injected from ITO (metal cathodes). Thus all of these three diodes are hole-only devices.[16] Furthermore, the work functions of ITO (4.6 eV) and Au (5.1 eV) are close to the highest occupied molecular orbital (HOMO) level (4.8 eV) of CuPc. Hence, ITO or Au acts as an Ohmic contact.[11,17] However, when Al (4.2 eV) or Mg (3.7 eV) serves as a cathode, Al or Mg acts as the Schottky contact because the contact barriers between the work function of Al or Mg and the HOMO level of CuPc are more than 0.6 eV.[17,18]

Based on the above results, when the organic diode is forward-biased (Fig. 2(c)), holes will be injected into CuPc from ITO, which means that only a positive SCLC capacitance $C_{\rm S0}$ exists.[13] When the organic diode is reverse-biased (Fig. 2(d)), holes will be injected from the metal cathodes. If Au is used as the cathode, only a reverse SCLC capacitance $C_{\rm S1}$ exists too. If Al or Mg acts as the cathode, holes will first tunnel through a triangular energy barrier (Schottky junction)[16] and then are injected into CuPc. As a result, there are two kinds of capacitance: reverse Schottky capacitance C_j and reverse SCLC capacitance $C_{\rm S2}$.[14,15] Thus, Fig. 3 shows the small-signal equivalent model of the organic Schottky diode we established (Fig. 3(a): Au acts as cathode, Fig. 3(b): Al or Mg acts as cathode). D_0 is the ideal diode, R_d is the dead resistance, C_j is the reverse Schottky junction capacitance, $C_{\rm S}$ ($C_{\rm S0}$, $C_{\rm S1}$, $C_{\rm S2}$) is the SCLC capacitance.

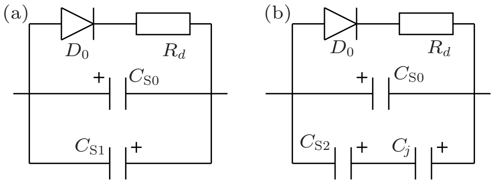

Fig. 3. The small-signal equivalent model of the organic Schottky diode. (a) Au acts as cathode. (b) Al or Mg acts as cathode.

In order to investigate the reverse capacitance of the organic Schottky diode, we try to obtain the reverse equivalent circuit and to calculate the reverse capacitances $C_{\rm Metal}$ with different cathodes. In Fig. 3, when the organic Schottky diode is forward-biased, positive SCLC capacitance $C_{\rm S0}$ is the only capacitance present. When the organic Schottky diode is reverse-biased, as for the case of the Au cathode, the reverse SCLC capacitance $C_{\rm S1}$ is the only capacitance. For the case of Al or Mg used as the cathode, the reverse capacitance includes the reverse Schottky junction capacitance C_j and the reverse SCLC capacitance $C_{\rm S2}$.

Figure 4(a) schematically shows an input-output from the oscilloscope (input: curve 1, output: curve 2). Figures 4(b), 4(c) and 4(d) show the negative output $V_{\rm out-}$ measured versus positive input $V_{\rm in+}$ at different frequencies (4 kHz, 6 kHz, 8 kHz, 10 kHz, 20 kHz) (negative input $V_{\rm in-}$ equals -2 V) with different metal cathodes (Mg, Al, Au). We find that when the frequency of the ac input is less than 10 kHz, negative output voltage $V_{\rm out-}$ only depends on the frequency of ac input. As we know, the positive SCLC capacitance $C_{\rm S0}$ could affect the negative output $V_{\rm out-}$ because when an organic Schottky diode is forward-biased, $C_{\rm S0}$ acts as a capacitor, and then, when the diode is reverse-biased, the $C_{\rm S0}$ serves as an extra power source by discharging. This means that the effect of $C_{\rm S0}$ could be ignored when the frequency of the input is below 10 kHz. Then we can deduce the reverse equivalent circuit as load resistance R in series with reverse SCLC capacitance $C_{\rm S1}$ when Au acts as the cathode (Fig. 5(a)) or R in series with reverse Schottky junction capacitance C_j and reverse SCLC capacitance $C_{\rm S2}$ when Mg or Al acts as the cathode (Fig. 5(b)).

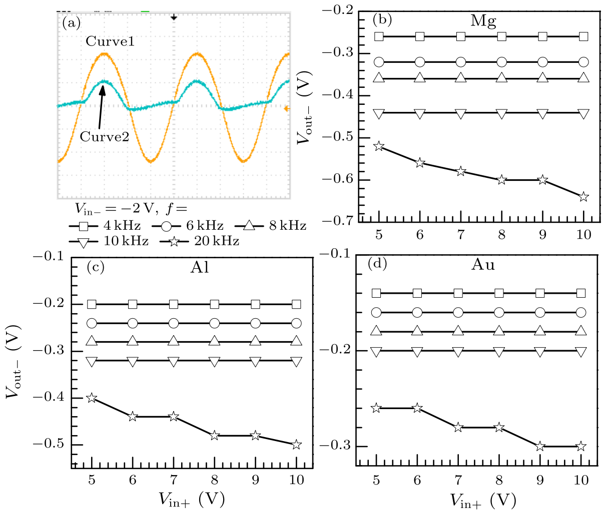

Fig. 4. (a) Input-output schematic diagram. (b) Negative output voltage $V_{\rm out-}$ measured as a function of positive input voltage $V_{\rm in+}$ at different frequencies (4 kHz, 6 kHz, 8 kHz, 10 kHz, 20 kHz) and negative input voltage $V_{\rm in-}$ equal to -2 V when the cathode is Mg. (c) Al acts as cathode. (d) Au acts as cathode.

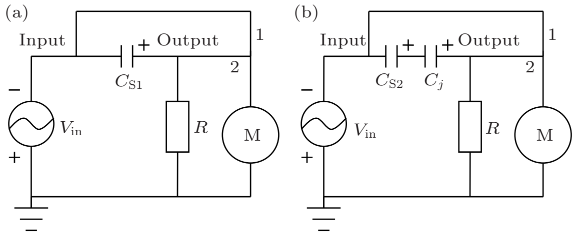

Fig. 5. Reverse equivalent circuit diagram. (a) Au acts as cathode. (b) Al or Mg acts as cathode.

According to the reverse equivalent circuits shown in Fig. 5, we can calculate the value of reverse capacitance $C_{\rm Metal}$ with the following formulas:

$$X_{C_{\rm Metal}} = 1/2\pi f C_{\rm Metal}, \tag{1}$$

$$R_0 = \sqrt{R^2 + X^2_{C_{\rm Metal}}}, \tag{2}$$

$$V_{\rm out-} = R/R_0 V_{\rm in-}, \tag{3}$$

where $X_{C_{\rm Metal}}$ is the impedance of the reverse capacitance, f is the frequency of input, R_0 is the total resistance of the reverse equivalent circuit, load resistor $R = 100\,\Omega$, $V_{\rm out-}$ and $V_{\rm in-}$ are recorded by the oscilloscope. According to Eqs. (1), (2) and (3), we obtain the frequency-reverse capacitance ($F - C_{\rm Metal}$) characteristics with different metal cathodes (Au, Al, Mg), as shown in Fig. 6. It is found that the reverse capacitance $C_{\rm Metal}$ is $C_{\rm Mg} > C_{\rm Al} > C_{\rm Au}$ at the same frequency.

The reverse capacitance $C_{\rm Metal}$ of the organic Schottky diode is analyzed. Based on the small-signal equivalent model of the organic Schottky diode shown in Fig. 3, when Au serves as the cathode, $C_{\rm Au} = C_{\rm S1}$, as shown in Fig. 3(a), and when Al or Mg is used as the cathode in Fig. 3(b), then $\frac{1}{C_{\rm Metal}} = \frac{1}{C_{j-\rm Metal}} + \frac{1}{C_{\rm S2-Metal}}$ ($C_{j-\rm Metal}$: reverse Schottky capacitance, $C_{\rm S2-Metal}$: reverse SCLC capacitance).

For the case of Au serving as the cathode, $C_{\rm Au}$ can be calculated by[13]

$$C_{\rm Au} = A\varepsilon/d, \tag{4}$$

where A is the active area of the organic diode ($A = 0.12\,{\rm cm}^2$), d is the thickness of CuPc film ($d = 40$ nm), and according to the previous report for CuPc[19] we assume the dielectric constant of CuPc, i.e. $\varepsilon_{\rm CuPc} = 4.5 \times 10^{-11}$ F/m. Based on Eq. (4), we obtain the calculated $C_{\rm Au} = 13.5$ nF, which agrees with $C_{\rm Au} = 15.7$ nF when $f = 10$ kHz in our experiment, as shown in Fig. 6.

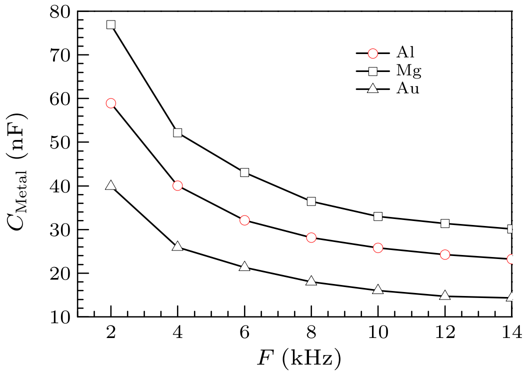

Fig. 6. $F - C_{\rm Metal}$ characteristics with different metal cathodes (Au, Al, Mg).

For the case of Al or Mg used as the cathode, $\frac{1}{C_{\rm Metal}} = \frac{1}{C_{j-\rm Metal}} + \frac{1}{C_{\rm S2-Metal}}$, both the reverse Schottky capacitance $C_{j-\rm Metal}$ and the reverse SCLC capacitance $C_{\mathrm{S2-Metal}}$ contribute to the reverse capacitance C_{Metal}. For the reverse Schottky capacitance $C_{j-\mathrm{Metal}}$, we can calculate it based on the standard Mott–Schottky relationship[15]

$$\frac{1}{C^2} = \frac{2(V_{\mathrm{in}} - V)}{e\varepsilon_1\varepsilon_0 N},$$

where $C = C_{j-\mathrm{Metal}}/A_{\mathrm{Metal}}$ is the unit-area Schottky capacitance, V_{in} is the intercept voltage, V is the voltage supplied ($V = -2\,\mathrm{V}$), ε_1 is the dielectric constant, ε_0 is the vacuum permittivity, k is the Boltzmann constant, and N is the ionized carrier density.

According to Fig. 2(b), the Schottky contact barriers between the work function of Al or Mg and the HOMO level of CuPc are 0.6 eV and 1.1 eV, respectively, which means the intercept voltage $V_{\mathrm{in-Mg}} > V_{\mathrm{in-Al}}$.[20] Moreover, noticing the active area of the organic diode $A_{\mathrm{Mg}} = A_{\mathrm{Al}}$, we can obtain $C_{j-\mathrm{Mg}} < C_{j-\mathrm{Al}}$ by Eq. (5), which is in contradiction to our result $C_{\mathrm{Mg}} > C_{\mathrm{Al}}$ shown in Fig. 6. These show that $C_{j-\mathrm{Metal}}$ cannot be responsible for the reverse capacitance C_{Metal}.

For the reverse SCLC capacitance $C_{\mathrm{S2-Metal}}$, according to Fig. 2(d), there is a triangular energy barrier (Schottky junction) when an organic diode is reverse-biased and Al or Mg acts as the cathode. Considering the width of triangular energy barrier W_{Metal}, we have $W_{\mathrm{Mg}} > W_{\mathrm{Al}}$. The effective thickness d_{Metal} of $C_{\mathrm{S2-Metal}}$ reads $d_{\mathrm{Metal}} = d - W_{\mathrm{Metal}}$ (d: thickness of CuPc film), so $d_{\mathrm{Al}} > d_{\mathrm{Mg}}$. Based on $C_{\mathrm{S2-Metal}} = A\varepsilon/d_{\mathrm{Metal}}$, we can realize $C_{\mathrm{S2-Mg}} > C_{\mathrm{S2-Al}}$. In addition, as we know, $C_{\mathrm{Au}} = A\varepsilon/d$ and $d > d_{\mathrm{Al}} > d_{\mathrm{Mg}}$. Hence, we obtain $C_{\mathrm{S2-Mg}} > C_{\mathrm{S2-Al}} > C_{\mathrm{Au}}$, which agrees with the result $C_{\mathrm{Mg}} > C_{\mathrm{Al}} > C_{\mathrm{Au}}$, as shown in Fig. 6. Based on the above results, it is considered that the reverse SCLC capacitance $C_{\mathrm{S2-Metal}}$ dominates the reverse capacitance C_{Metal} when Al or Mg acts as the cathode.

According to our analysis, when an organic Schottky diode is working in a high frequency ac circuit, positive SCLC capacitance is the only positive capacitance and the reverse SCLC capacitance is the dominating reverse capacitance (Fig. 5(b)). The positive SCLC capacitance acts as a capacitor when the organic Schottky diode is forward-biased, and then, when the diode is reverse-biased, positive SCLC capacitance serves as an extra power source by discharging. For the reverse SCLC capacitance, when the organic Schottky diode is reverse-biased, the reverse equivalent circuit will be the load resistor R in series with the reverse SCLC capacitance, based on $X_C = 1/2\pi cf$, where C represents the reverse capacitance. We can find that the lower reverse SCLC capacitance will lead to the higher frequency characteristics of the organic Schottky diode. Thus, SCLC capacitance C_{S} is the main roadblock for the implementation of high-frequency organic Schottky diodes.

In conclusion, we have investigated the capacitance of organic Schottky diodes by an organic small-signal equivalent model we have established. According to the result that reverse capctitance C_{Metal} reads $C_{\mathrm{Mg}} > C_{\mathrm{Al}} > C_{\mathrm{Au}}$ at the same frequency, the SCLC capacitance C_{S} instead of C_j is found to dominate the reverse capacitance of organic Schottky diodes, which means that the SCLC capacitance C_{S} is the main limit for the higher frequency characteristics of organic Schottky diodes.

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