Electrical Hole Transport Properties of an Ambipolar Organic Compound with Zn-Atoms on a Crystalline Silicon Heterostructure

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ABSTRACT In this paper, we investigate the electrical hole transport properties of an organic/inorganic heterostructure consisting of a thin organic film, that combines hole and electron conducting molecules around a bridging Zn-atom, deposited on top of an n-type crystalline silicon substrate. Current-voltage characteristics and capacitance voltage measurements have been used for the determination of the organic layer dielectric and hole conduction parameters.

INDEX TERMS Organic/inorganic heterodiode, capacitance-voltage measurement spectroscopy, charge carrier mobility, electronic energy levels; dielectric constant.

I. INTRODUCTION

Molecular electronics is based on the synthesis of single molecules or groups of molecules which allow to build, on a nanometer scale, single blocks that work as active layers in electronic components [1]. Devices based on a single molecule have the potential to combine the capability of high-density devices with low power consumption and can be fabricated with simple deposition techniques, such as spin-coating, ink-jet printing and drop-casting [2]. Normally, in organic electronic devices, based either on a single [3] or on a double active layer [4], the holes and electrons are transported in geometrically separated materials. Recently, new types of ambipolar molecules [5] and polymers [6] allow transporting electrons and holes within the same unit. This enables new concepts for organic electronic devices.

The small molecule used in this work is $Zn(OC)_2$, a combination between a hole transport molecule (carbazole) and an electron transport molecule (oxadiazole), joined by means of a central Zn atom [7]. In order to analyze the hole transport properties of the organic layer, a heterostructure between the Zn-organic compound complex and crystalline silicon (c-Si) has been prepared.

II. EXPERIMENT

Organic/inorganic hetero-diodes have been prepared by drop-casting of $Zn(OC)_2$ small molecules in tetrachloroethane solution on top of n-type phosphorous doped crystalline silicon (c-Si) substrates (<110> oriented with a resistivity of 7–13 Ω cm). The resulting organic layer film thickness (d) was 150 nm. The natural oxide on the c-Si substrates has been removed with a 2 s dip in 48% HF before the drop-casting. Contacts have been fabricated by silver paste dots and the successful realization of a good ohmic back contact has been checked by the characterization of a reference structure without organic top layer. The detailed fabrication process of this type of hetero-diode and the synthesis of this new type of small molecule is reported in [7]. The cross-section of the organic/inorganic heterojunction device is shown in the inset of Fig. 1 (the top contact area (A) was 0.064 cm^2). The current–voltage characteristics of the device have been measured under dark condition at room temperature, using a Keithley 2400 source-measurement unit. The capacitance - voltage characterization has been done using an HP 4109 impedance/gain-phase analyzer in the frequency range between 100 Hz to 1 MHz and with varying dc
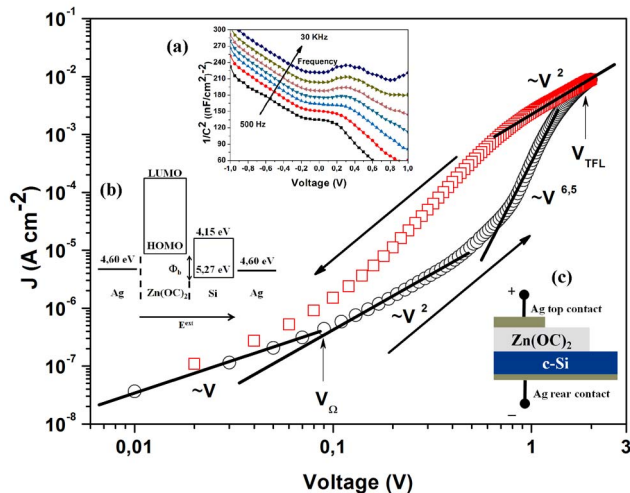
FIGURE 1. Current density-voltage characteristics of the heterojunction between n-type c-Si and Zn(OC)$_2$ layer at room temperature. (a) Mott–Schottky plot, measured from 500 Hz up to 30 KHz. (b) and (c) are the band-diagram of the hetero-diode and the device cross section, respectively. The energy levels are referred to the vacuum level.

bias voltage values between -1 V to 1.5 V with an ac-signal amplitude of 50 mV.

III. RESULTS AND DISCUSSION

At low frequencies and under reverse bias condition, the ac equivalent circuit of the heterostructure is simply composed by a series connection of the depletion capacitance (C$_{depl}$) of the silicon substrate and the geometrical capacitance (C$_g$) of the organic layer. The value of the capacitance due to the traps in the organic layer is negligible compared to C$_g$. In Fig. 1 the current density-voltage (J-V) and the Mott-Schottky plot of the Zn(OC)$_2$/c-Si heterostructure are shown. From the Mott-Schottky analysis of the capacitance-voltage (C-V) measurements, as shown in Fig 1(a), a value of the dopant concentration of the silicon substrate (N$_D$) of 4.32×10^{14} cm^{-3} [8] has been deduced in the reverse bias voltage range between -0.2 and -0.9 V. This is in good agreement with the nominal silicon wafer resistivity. The linear slope in the reverse bias region changes to a steeper slope in the forward bias regime due to the presence of the acceptor levels (with N$_A$ concentration) in the forbidden band gap of the silicon, which results in a modification of the equivalent doping concentration to N$_D$-N$_A$ = 2.06×10^{14} cm^{-3}.

As reported by Goodman [9], the frequency dependence of the Mott-Schottky plot, shown in Fig. 1(a), can be explained by the influence of the series resistance of the Zn(OC)$_2$/c-Si heterodiode. It is found that the extracted built-in voltage (V$_{bi}$) increases with increasing measurement frequency. A similar frequency dependence, at low and for intermediate frequencies, is also reported by Stallinga *et al.* [10] for a Metal-Insulator-Semiconductor structure with an organic film as insulating layer. In order to obtain a real value of the barrier height (Φ$_b$) at the Zn(OC)$_2$/n-Si interface, it is necessary to approximate the extracted voltage intercept (V*) in the relation: V* = f(ω^2),

where $\omega = 2\pi f$ and f is the frequency. The zero frequency intercept gives an approximation value [11] of the barrier height of about 0.84 eV. As a consequence, the energetic position of the highest occupied molecular orbitals (HOMO) level for the organic layer can be estimated to have a value of 4.47 eV. Thus, the top metal contact works as an ohmic contact for the holes, while for the electrons there is an injection barrier of Φ = 0.55 eV at the c-Si/top metal interface, while at the interface between the organic layer and the c-Si the electrons are blocked.

The value of C$_g$ can be estimated, taking the value of C$_{depl}$ at 500 Hz and zero applied bias voltage into account. Once known the thickness of the organic layer, its relative dielectric constant (ε_r) has been estimated to have a value of 4.66.

In Fig. 1 the voltage dependence of the current density suggests that the dominant conduction mechanism in the organic layer at intermediate voltages is the space charge limited current (SCLC) [12]. At low voltages, the curve follows an ohmic (linear) regime, due to the presence of the thermally generated free carriers (n$_0$), related to the shallow defect states, that at room temperature do not act as effective charge traps. Given the voltage V$_\Omega$ = 0.1 V, at which the transition between the ohmic regime and the SCLC regime occurs, an estimation of n$_0$ is possible by using the equation: n$_0$ = V$_\Omega$ θ ε_r ε_0/(dq), where q is the electron charge. θ = n/(n+N$_t$) is the trap parameter which takes the effect of the traps on the charge carrier mobility into account. It is the ratio between the free injected charge carriers (n) and the trap density [12], because it can be assumed, that N$_t$ >> n. With increasing applied voltage, at V > V$_\Omega$, the injected hole concentration exceeds that of the thermally generated free carrier concentration and the SCLC current becomes dominant. Thus, the current density can be expressed as J$_1$ = 9/8$\theta\mu_h\varepsilon_0\varepsilon_r$V^{2}d^{-3}, where μ_h is the hole mobility and ε_0 is the dielectric constant of the vacuum. At high bias voltages, the current increases rapidly and reaches the trap-free regime value (θ = 1) at an applied bias V$_{TFL}$ = qN$_t$d^2$\varepsilon_0$$\varepsilon_r$, where N$_t$ = 2.13×10^{16} cm^{-3} is the density of traps and V$_{TFL}$ has a value of about 1.8 V. Therefore, the current density for bias voltages greater than 1.8 V can be expressed as J$_2$ = 9/8$\mu_h\varepsilon_0\varepsilon_r$V^{2}d^{-3}. θ can be estimated by the ratio between the J-V curve in the SCLC regime, J$_1$, and in the SCLC trap-free regime J$_2$, that θ= J$_1$/ J$_2$. The resulting value of θ is 2.47 $\times$ 10^{-2}. As a consequence, the density of the thermally generated free carriers has a value of 4.25×10^8 cm^{-3}. The resulting value of the hole mobility is 1.11 $\times$ 10^{-5} cm^2 V^{-1} s^{-1} in the free carrier regime. For V $<$ V$_{TFL}$, the effective charge carrier mobility μ_{eff} = $\theta\mu_h$ = 2.74$\times$ 10^{-7} cm^2 V^{-1} s^{-1}. This rather low value of μ_h is due to the structural disorder of the organic layer [13]. The long distance between two single transport units implies that the holes should have enough energy to hop between the delocalized states and then reach the interface. The hysteresis is due to a capacitive effect.

The frequency dependence of the capacitance at different bias voltages is shown in Fig. 2. In reverse bias (V $\leq$ 0 V), the charge amount due to the perturbation ac signal depends on
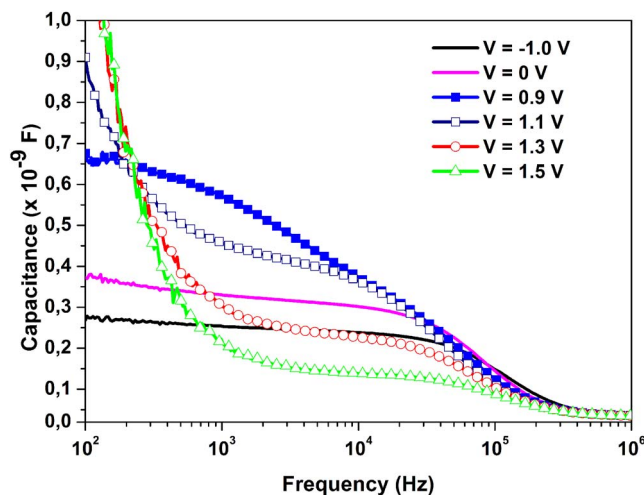
FIGURE 2. Measured capacitance as a function of the frequency at different applied voltage. In reverse bias V = −1.0 V, 0 V (solid line) and in forward bias V = 0.9 V, 1.1 V, 1.3 V, 1.5 V (solid line with symbols).
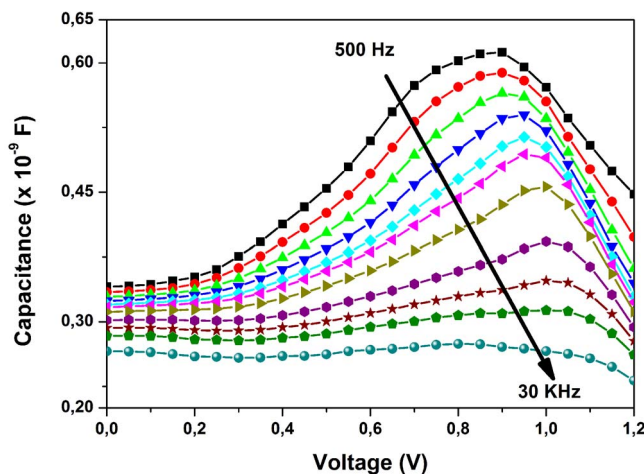

FIGURE 3. Room temperature capacitance-voltage characteristics of the Zn(OC)$_2$/n-Si heterojunction diode at frequencies between 500 Hz and 30 KHz.

the C$_{depl}$ of the silicon. The contribution of the capacitance of the organic layer is negligible. For larger values of the forward bias voltage (0 < V < 0.9 V) the injected holes, from the top metal contact, in the organic layer follow the external electric field (E^{ext}). The increase of the capacitance indicates a re-distribution of the injected carriers with a finite transit time [14]. In this voltage region, no charge carrier recombination has been observed. At still higher forward voltages (V > 0.9 V) the holes are injected into the silicon layer and the recombination becomes dominant [15]. The recombination process consumes the injected carriers, resulting in a rapid decrease of the capacitance values. The dependence of the capacitance on voltage at various frequencies is shown in Fig. 3. A marked peak is evident at V = V$_{bi}$ = 0.9 V.

In Fig. 3 the dependence of the C-V curves on the measurement frequency is shown. At high frequencies the carriers are not able to follow the ac signal, resulting in a capacitance value, almost independent of the applied voltage.

IV. CONCLUSION

An electrical characterization of the Zn-organic compound and c-Si heterostructure has been made by current-voltage and capacitance measurements. The barrier heights at the interfaces and the value of the dielectric constant for the organic layer (ε$_r$ = 4.66) have been determined. The determined low value of the HOMO level energy (4.44 eV) allows to form a relatively good ohmic contact with the Ag front contact. The dominating electrical conduction mechanism for holes is the trap-controlled space charge limited current. The high value of the density of the traps of 2.13 × 10^{16} cm^{-3} results in a low value of the hole mobility of 2.74 × 10^{-7} cm^2 V^{-1} s^{-1} which increases up to a value of 1.11 × 10^{-5} when all traps are filled.

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