

# Frequency dependent interface state properties of a Schottky device based on perylene-monoimide deposited on n-type silicon by spin coating technique

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## ABSTRACT

We have reported a detailed investigation of frequency dependent properties of the Au/perylene-monoimide (PMI)/n-Si Schottky diodes in this study. Schottky diodes based on PMI have been fabricated by spin coating method. The capacitance–voltage (*C–V*) and conductance–voltage (*G–V*) characteristics have been measured in the frequency range from 30 kHz to 1 MHz at room temperature. The values of measured capacitance  $C_m$  and conductance  $G_m$  under both reverse and forward bias have been corrected for the effect of series resistance to obtain the real diode capacitance and the conductance values. The density of interface states ( $D_{it}$ ) distribution profiles as a function of frequency has been extracted from the corrected *C–V* and *G–V* measurements. Interface trap states of the PMI/n-Si Schottky device have decreased by increasing the applied frequency and were found to be  $8.13 \times 10^{11}$  and  $1.75 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$  for 30 kHz and 1 MHz, respectively.

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## 1. Introduction

Recently, considerable studies have been devoted to the investigation of organic semiconductor devices based on perylene and its derivatives because of their promising applications in organic electronics such as field effect transistors [1], light emitting devices [2–4], photovoltaic devices [5], laser dyes [6], Schottky diodes [7–10]. Perylene-monoimide (PMI) dyes have been used for dye sensitized solar cells (DSSCs) with overall conversion efficiency of 1.61% [11] and 2.6% [12]. One of the most important potential applications is organic radio frequency identification (RFID) tags, which are better than silicon RFID tags [13,14] in aspect 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 wide implementation of high-frequency RFID tags based on organic semiconductors.

The performance and reliability of organic based Schottky barrier diodes especially depend on the formation of interfacial layer at metal–semiconductor (MS) interface, the level of interface states ( $D_{it}$ ) at organic layer/Si interface, series resistance ( $R_s$ ) of devices, and inhomogeneities of the Schottky barrier formation at MS interface [15–18]. The existence of such an organic layer can have a strong influence on the diode characteristics as well as the interface state density  $D_{it}$ , barrier height  $\Phi_B$ , fermi energy  $E_F$  and donor carrier concentration  $N_D$  [19–22]. Therefore, it is very important to determine the interfacial properties of an organic based Schottky diode [23–25].

A combination of the forward and reverse bias *C–V* and *G–V* measurements provides important information not only about the semiconductor layer, e.g., doping density and bulk mobility [26] but also on the interface between semiconductor and gate dielectric [26,27], e.g., the density of states of

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interface traps [28]. In general, the  $C-V$  and  $G-V$  plots in the idealized case are considered as frequency-independent [16–18]. However, this idealized case is often disturbed due to the presence of an interfacial layer between the contact materials and of the interface states at semiconductor-interfacial layer [16–18]. These interface states usually cause a bias shift and frequency dispersion of the capacitance–voltage ( $C-V$ ) characteristics [17,18]. At high frequencies ( $f \geq 500$  kHz), the charges at the interface states cannot follow an ac signal. In contrary, at low frequencies, about at 100 Hz, the charges can easily follow an ac signal. Therefore, the frequency dependent electrical characteristics are quite important to obtain the accurate and reliable results. One of the measurement technique is Hill–Coleman method [29] for determining the interface state density. Kavasoglu et al. [20] obtained Au/PVP/p-Si structure by addition of a poly(4-vinyl phenol) by spin coating method on top of the p-type Si substrate. They measured capacitance–voltage ( $C-V$ ) characteristics of Au/PVP/p-Si structure in the frequency range from 1 kHz to 1 MHz and determined  $D_{it}$  values varying between  $10^{12}$  and  $10^{13}$   $\text{eV}^{-1} \text{cm}^{-2}$ . Yakuphanoglu et al. [21] investigated the capacitance–voltage characteristics of Au/methylene blue/n-Si diode under various frequencies. The interface state density for the diode was found to be  $3.25 \times 10^{12}$   $\text{eV}^{-1} \text{cm}^{-2}$ .

In the previous work, we have reported the effect of the use of an organic film on the modification of electrical properties of Si Schottky diode [8–10]. For this aim, a detailed analysis of the current–voltage ( $I-V$ ) characteristics of organic Schottky diodes based on perylene-monoimide (PMI) at a wide temperature range between 75 and 300 K has been investigated. The goal of this study is to investigate the frequency dependent electrical and interface state properties of Au/PMI/n-Si Schottky diode using capacitance–voltage ( $C-V$ ) and conductance–voltage ( $G-V$ ) measurements at a wide frequency range from 30 kHz to 1 MHz. To obtain the real diode capacitance and conductance values, the capacitance ( $C_m$ ) and conductance ( $G_m$ ) measured as a function of frequency under both reverse and forward bias were corrected taking into account the effect of series resistance.

## 2. Experimental details

The semiconductor substrates used here are n-type P-doped Si single crystals, with a (1 0 0) surface orientation,  $20 \Omega \text{cm}$  resistivity and  $380 \mu\text{m}$  thickness. The Si wafer is initially degreased with organic solvents like trichloroethylene, acetone and methanol using ultrasonic agitation for 5 min to remove the contaminants and rinsed in deionized water and then dried in  $\text{N}_2$  flow. The wafer was chemically cleaned using the RCA cleaning procedure (i.e., a 10 min boil in  $\text{NH}_3 + \text{H}_2\text{O}_2 + 6\text{H}_2\text{O}$  followed by a 10 min boil in  $\text{HCl} + \text{H}_2\text{O}_2 + 6\text{H}_2\text{O}$ ) with the final dip in diluted HF for 60 s, and then rinsed in deionised water of resistivity of  $18 \text{M}\Omega \text{cm}$  with ultrasonic vibration and dried by high purity nitrogen. Immediately after surface cleaning, gold (Au) metal with a purity of 99.99% was thermally evaporated on the whole back surface of the wafer with a thickness of 150 nm under vacuum of approximately  $8 \times 10^{-4}$  Pa. Then, a heat treatment was performed at

$500^\circ\text{C}$  for 3 min in vacuum to obtain a low resistivity ohmic contact. Next, a PMI organic film was formed by spin coating method at a spinning rate of 1200 rpm with the duration time of 60 s using toluene solution (5 mg/ml) by using a Laurell Spin Coater. The morphology and the thickness of the PMI organic film layer strongly depend on the chemical nature of a substrate and the film has uniformly coated on the Si substrate. The molecular structure of PMI is given in Fig. 1(a). The PMI was synthesized according to the previously published procedures [30,31]. Next, Schottky contacts were deposited on this organic film with a diameter of  $2 \times 10^{-3}$  m and a thickness of 150 nm using a metal shadow mask by evaporating 99.99% purity gold (Au) metal in  $8 \times 10^{-4}$  Pa vacuum having an active area of  $A = 3.14 \times 10^{-6}$   $\text{m}^2$ . The schematic representation of the device is shown in Fig. 1(b). The capacitance–voltage ( $C-V$ ) and conductance–voltage ( $G-V$ ) measurements were performed at room temperature and in dark using a HP 4192A LF impedance analyzer (5 Hz–13 MHz).

## 3. Results and discussion

Fig. 2(a) and (b) represent the measured capacitance–voltage ( $C_m-V$ ) and conductance–voltage ( $G_m-V$ ) measurements under both forward and reverse-bias voltages in the frequency range of 30 kHz–1 MHz at room temperature for Au/PMI/n-Si Schottky diode. As shown in Fig. 2(a) and (b), both  $C_m-V$  and  $G_m-V$  curves have three distinct regions called as accumulation, depletion and inversion at each frequency, verifying a typical metal–insulator–semiconductor (MIS) type Schottky barrier diodes behavior. The values of  $C_m$  and  $G_m$  are dependent on both bias voltage and also on frequency. The changes in  $C_m$  and  $G_m$  occur especially in the depletion and accumulation

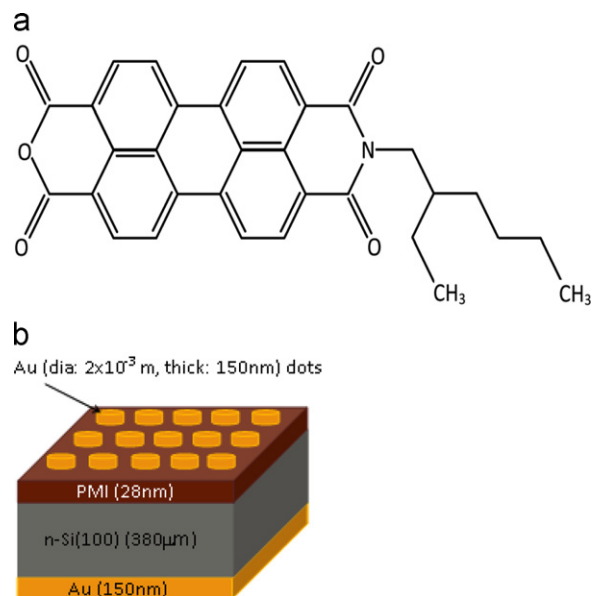


Fig. 1. (a) Molecular structure of a perylene-monoimide organic compound, and (b) schematic diagram of the configuration of Au/PMI/n-Si Schottky diode for electrical characterization.

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