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The conductance and capacitance–frequency characteristics of Au/pyronine-B/p-type Si/Al contacts

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Abstract

The rectifying junction characteristics of the organic compound pyronine-B (PYR-B) film on a p-type Si substrate have been studied. The PYR-B has been evaporated onto the top of p-Si surface. The barrier height and ideality factor values of 0.67 ± 0.02 eV and 2.02 ± 0.03 for this structure have been obtained from the forward bias current–voltage (*I–V*) characteristics. The energy distribution of the interface states and their relaxation time have been determined from the forward bias capacitance–frequency and conductance–frequency characteristics in the energy range of $((0.42 \pm 0.02) - E_v)$–$((0.66 \pm 0.02) - E_v)$ eV. The interface state density values ranges from $(4.21 \pm 0.14) \times 10^{13}$ to $(3.82 \pm 0.24) \times 10^{13}$ cm^{-2} eV^{-1}. Furthermore, the relaxation time ranges from $(1.65 \pm 0.23) \times 10^{-5}$ to $(8.12 \pm 0.21) \times 10^{-4}$ s and shows an exponential rise with bias from the top of the valance band towards the midgap.

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1. Introduction

The electrical properties of semiconductor–insulator interfaces have been widely studied, both for their basic physical properties and for their technological applications to electronic devices. Semiconductors such as Si have application to a wide variety of high-frequency (HF) metal/oxide/semiconductor (MOS) devices. The fabrication of such devices depends on having both a good insulating oxide and a low interface state density between the oxide and semiconductor [1–12]. Furthermore, the motivation behind the use of the metal/interfacial layer/inorganic semiconductor structures as a voltage-variable capacitor has been fabrication of stable and high performance devices and integrated circuits [12–22]. In the present study, Au/PYR-B/p-Si/Al structures are directly formed evaporating the organic compound PYR-B onto the top p-Si surface. Our purpose is to determine experimentally whether or not the Au/PYR-B/p-Si/Al structure behaves like metal/oxide/semiconductor devices due to PYR-B layer between Au and p-Si. The electrical and photoelectrical properties of polymeric [13–17] and nonpolymeric organic compounds [18–23] have been the investigations subject for more than the last two and three decades. Due to stability of nonpolymeric organic compounds, they have been employed particularly in the electronics devices [18–22].

The interface states and interfacial layer at the organic semiconductor–inorganic semiconductor structures play an important role in the determination of the barrier height of the devices. The organic/inorganic semiconductor diodes can be a sensitive probe useful in establishing processes for minimizing surface states, surface damage, and contamination which may ultimately increase the quality of devices fabricated using the semiconductor. The organic/inorganic semiconductor device is particularly suited to inorganic semiconductor surface analysis [12–22]. The characteristic parameters of the fabricated nonpolymeric organic compound Au/PYR-B/p-Si/Al structures were calculated using the forward bias current–voltage (*I–V*), forward bias capacitance–frequency (*C–f*) and forward bias conductance–frequency (*G–f*) measurements. The forward bias *C–f* and *G–f* measurements give the important information

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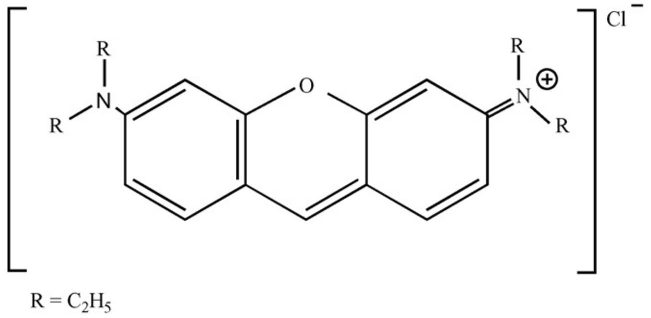

Fig. 1. Molecular structure of the Pyronine-B.

about the interface state energy distribution of the Au/PYR-B/p-Si/Al structures. In generally, the *C–f* and *G–f* plots in the idealized case are frequency independent [1–12,24]. However, this idealized case is often disturbed due to the presence of an interfacial layer between the contact materials and interface states at the interfacial layer/semiconductor interface [1–12,24].

The PYR-B is a xanthene-type molecule and has a photophysical fluoresence quantum yield of about 0.56 in alcohols [23]. Since pyronine-B has a conjugation in its structure, it is a good conductive compound. The molecular structure of PYR-B is given in Fig. 1. As can be seen from the figure, two electrical structures are possible in which the conjugation is totally different, one where the oxygen assumes positive charge and in the other possible structure the nitrogen assumes positive charge. However, because the nitrogen is less electronegative than oxygen, the former can support a positive charge more easily than the latter, and therefore the structure with positive nitrogen is the more likely one [25]. Most conducting organic compounds are of p-type because of the great number of acceptor states that inject holes into the valence band and they have a concentration in the range 10^{15}–10^{17} cm^{-3} [25–27]. An important property of organic semiconductors like PYR-B is that the minimum energy for the formation of a pair of separated free electron and hole, i.e., the transport gap $E_{\text{trans}} = E_{\text{LUMO trans}} - E_{\text{HOMO trans}}$ is found to be considerably larger than the optical band gap involving exciton formation. The transport gap can be determined from the energy separation of the center of mass of the HOMO and LUMO level recorded by photoemission and inverse photoemission spectroscopy, respectively, and subtracting from this value the vibrational contribution and the difference between bulk and surface polarization [21,25]. Where HOMO is the highest occupied molecular orbital, the equivalent of the top of the valence band, and LUMO is the lowest unoccupied molecular orbital, the equivalent of the bottom of the conduction band.

2. Experimental procedure

The samples were prepared using mirror cleaned and polished (as received from the manufacturer) p-type Si wafers with (1 0 0) orientation and 5–10 Ω cm resistivity. The wafer was chemically cleaned using the RCA cleaning procedure [i.e., a 10 min boil in $NH_4OH + H_2O_2 + 6H_2O$ followed by a 10 min boil in $HCl + H_2O_2 + 6H_2O$]. The ohmic contact was made by evaporating Al on the back of the substrate in the vacuum system of 10^{-5} Torr, followed by a temperature treatment at 570 °C for 3 min in N_2 atmosphere. The native oxide on the front surface of the substrate was removed in $HF:H_2O$ (1:10) solution and finally the wafer was rinsed in deionized water for 30 s before forming organic layer on the p-type Si substrate. The PYR-B has directly been evaporated onto the top p-Si surface. The deposition rate of the PYR-B was between 6 and 9 nm s^{-1}, as determined using a quartz-crystal thickness monitor. The distance from the evaporation source to the Si substrates was maintained at 12 cm and the substrate temperature was about 30 °C. The thickness of the pyronine-B film on the substrate changed from the diode to diode in the range of 110–130 nm, and the film thickness was uniform across the surface area of each dot (the diode). Finally, top metal contact, Au, was deposited using either filament through a shadow mask in the vacuum system of 10^{-5} Torr. In this way, an Au/PYR-B/p-Si/Al diode was obtained. The area of circular Schottky contact was 1.43×10^{-2} cm^2. All metallic surfaces were cleaned by acetone and methanol before processes. The *I–V* and *C–V–f* measurements of the device were performed using a Keithley 487 Picoammeter/Voltage Source and a HP 4192A *LF* Impedance Analyzer, respectively, at room temperature in dark.

3. Results and discussion

3.1. The current–voltage characteristics

When a metal/semiconductor contact with a thin interfacial layer is considered, it is assumed that the forward bias current of the device is due to thermionic emission current and it can be expressed as [1]:

$$I = I_0 \exp\left(\frac{qV}{nkT}\right)\left[1 - \exp\left(-\frac{qV}{kT}\right)\right], \tag{1}$$

where

$$I_0 = AA^{*}T^2 \exp\left(-\frac{q\Phi_{\text{b},0}}{kT}\right), \tag{2}$$

is the saturation current density, $\Phi_{\text{b},0}$ the barrier height at zero bias, A^* the effective Richardson constant and equals to 32 A cm^{-2} K^2 for p-type Si, A the diode area, n is an ideality factor and is a measure of conformity of the diode to pure thermionic emission and it is determined from the slope of the straight line region of the forward bias ln *I–V* characteristics according to Eq. (1).

The electrical characteristics of five devices (the Au dots onto the PYR-B/p-Si substrate) were analyzed, and the standard error for the values of the experimentally derived quantities of the devices was calculated. Fig. 2 shows the forward and reverse current–voltage characteristics of one of the Au/PYR-B/p-Si/Al structures. We have calculated the