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Dielectric, conduction and interface properties of Au/Pc/p-Si Schottky barrier diode

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ABSTRACT

The dielectric properties and the ability of binuclear zinc(II) phthalocyanine of clamshell type compound in passivating silicon (Si) surfaces is studied by fabricating metal–insulator–semiconductor (MIS) capacitors. The frequency and temperature dependence of the dielectric constant were discussed in the light of Koops model and hopping conduction mechanism. A detailed study of the effect of temperature on the ac conductivity of MIS structure at the temperatures between 300 K and 460 K was carried out. Based on the existing theories of ac conduction, it has been concluded that for low frequency region the dominant conduction mechanism in the sample is quantum mechanical tunneling at all temperatures, whereas for intermediate frequency region multihopping process is the dominant conduction mechanism. At higher frequencies, the behavior and the values of index *s* reveal a free band conduction mechanism. Interface properties of the fabricated MIS structure were investigated by means of conductance–voltage (G_M–V_G) and the combination of low frequency and high frequency capacitance–voltage (C_M–V_G) measurements at various fixed frequencies. The values of D_{it} obtained from conductance and high–low frequency capacitance measurements are 4.25×10^{11} eV^{-1} cm^{-2} and 4.90×10^{11} eV^{-1} cm^{-2}, respectively. This indicates the consistency of both the methods. The observed peaks in the G_M–V_G characteristics indicated that the losses are predominantly due to interface states.

1. Introduction

In the fields of electronics and optoelectronics, organic semiconducting materials are very promising candidates for future technology of thin layers. Among them, phthalocyanines (Pcs) and its derivatives have attracted much attention in the past decades and found applications in novel electronic and photonic devices, such as junction diodes [1], organic light emitting diodes (OLEDs) [2,3], optical power limiting [4], photovoltaic, solar and fuel cells [5,6] and gas-sensing devices [7–9]. One of the most interesting features of the Pc molecules is that their physical and chemical properties such as, the band gap, valence and conduction band energies, charge transport mechanism, as well as the solubility can be freely altered via incorporation of different metal atoms at the center of the phthalocyanine ring or by changing the nature of the substituents on the periphery of the macrocyclic ring [10]. However the incorporation of organic molecules in the electronic devices shows still serious stability and processability limitations. At this stage one of the main needs is to find new stable organic semiconducting materials [11]. It is well understood that stable, low leakage and high permittivity dielectric thin films are required for fabrication of novel microelectronics devices. Recently, we have synthesized many kinds of phthalocyanine derivatives for developing new electronic, optoelectronic and gas sensing devices using their unique functions [12–14].

In the present work, we focused on studying the potentiality of the Pc film for use in Au/insulator/p-Si Schottky barrier diode as insulator layer. For this purpose, a novel binuclear zinc(II) phthalocyanine of the clamshell type has been synthesized. Thus, a Schottky barrier diode using this phthalocyanine compound has been fabricated. The charge transport mechanism and dielectric parameters determined from capacitance–voltage (C_M–V_G), conductance–voltage (G_M–V_G) and frequency–impedance (*f*–*Z*) measurements for Au/Pc/p-Si MIS capacitors in the frequency range between 20 Hz and 2×10^6 Hz at different temperatures.

2. Experimental details

The substrates used to prepare the MIS structure were p type (1 0 0) oriented silicon wafers with resistivity in the 8–10 Ω cm range. The wafer was chemically cleaned using the RCA cleaning procedure (i.e. a 10 min boil in $NH_4 + H_2O_2 + 6H_2O$ followed by a

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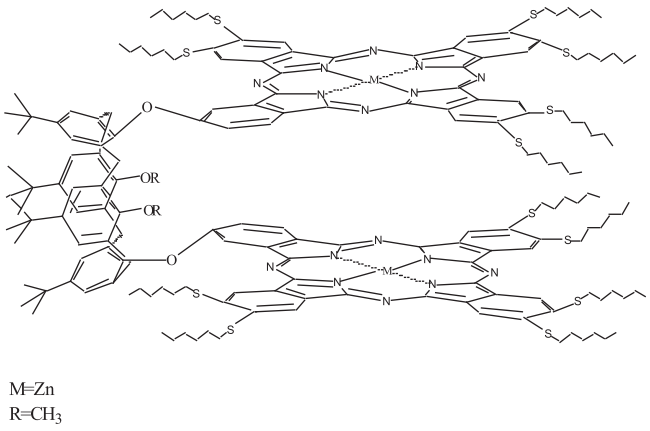

Fig. 1. The structural formula of binuclear zinc(II) phthalocyanine of clamshell type.

10 min boil in $HCl + H_2O_2 + 6H_2O$). After surface cleaning, Al metal with high purity (99.999%) was thermally evaporated on the substrate at pressure of 1.5×10^{-5} mbar in thermal evaporation system (Edwards Auto 500), followed by a temperature treatment at 450 °C for 5 min in N_2 atmosphere. The native oxide on the polished surface of the substrates was removed in HF/H_2O (1:10) solution and finally was rinsed in de-ionized water for 20 s before forming Pc layer on the p-type Si substrate. The synthesis procedure of the Pc molecule, shown in Fig. 1, was described in [15]. The purification of the compound was accomplished successfully as described in Ref. [15]. TLC, elemental analysis, mass and NMR spectra showed clearly that the compound was pure enough. Thin films of the compound were deposited onto a previously well cleaned Si substrate by spinning a small volume of the spreading solution. The spreading solution was prepared by dissolving compounds in DMF at concentrations of 5×10^{-3} M. Twenty microliters of this solution was added with a glass pipette onto the p-Si substrate held onto spinner (Speciality Coatings Systems Inc., Model P6700 Series).

The substrate spun at 2000 rpm for 80 s and then the films were dried at 100 °C for 2 h to evaporate the solvent. Elipsometric technique was used to measure the thickness of the Pc film and it was found to be 40 nm. After spinning process, circular dots of 1 mm in diameter and 1500 Å thick Au contacts were deposited onto the Pc surface of the wafer through a metal shadow mask in high vacuum system in the pressure of 1.5×10^{-5} mbar. The C_M–V_G, G_M–V_G and impedance spectroscopy measurements were carried out in the frequency range, 20 Hz to 2×10^6 Hz, and in the temperature range from 300 K to 460 K. During the measurement, the temperature of the sample was controlled with a lakeshore temperature controller. All the measurements were performed under 10^{-3} mbar.

3. Results and discussion

3.1. Dielectric properties of the Au/Pc/p-Si/Al diode

The components of the complex dielectric function, $\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$, were obtained from the measured impedance spectra using the expression [16],

$$\varepsilon^* = \frac{1}{j\omega C_0 Z^*} = \varepsilon'(\omega) - j\varepsilon''(\omega) \quad (1)$$

where Z^* is the measured impedance, C_0 is the capacitance of the empty measuring cell and ω is the angular frequency of the applied signal. The real part, $\varepsilon'(\omega)$, of the complex dielectric function is usually called the dielectric constant and the complex part, $\varepsilon''(\omega)$, the dielectric loss or dielectric loss factor.

The variation of real ($\varepsilon'(\omega)$) and imaginary ($\varepsilon''(\omega)$) parts of dielectric function as a function of frequency for Au/Pc/p-Si/Al

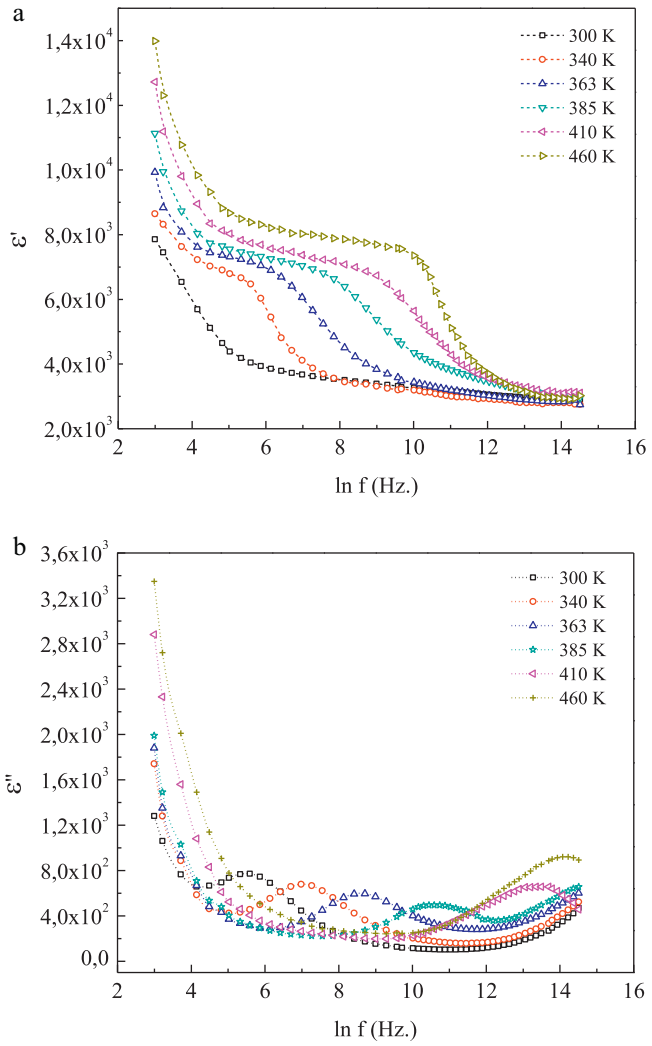

Fig. 2. The frequency dependence of the real (a) and imaginary (b) parts of dielectric function at different selected temperatures.

structure at different selected temperatures are illustrated in Fig. 2(a) and (b). As can be seen from Fig. 2(a), the observed frequency dependency reveals that the $\varepsilon'(\omega)$ exhibits non-Debye type relaxation for all temperatures. The real part of the $\varepsilon^*(\omega)$ displays a step decrease at the frequency where the dielectric loss shows a relaxation peak. As can be seen from this figure, the step in $\varepsilon'(\omega)$ and the relaxation peaks of the sample shift to higher frequencies with increasing temperature. It should be noticed that the height of the step, which is known as dielectric strength, is temperature independent. The presented data in Fig. 2(a) and (b) also shows that both $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ have large values at lower frequencies.

The behavior of $\varepsilon'(\omega)$ with the temperature, the step in $\varepsilon'(\omega)$ which shifts to higher frequencies with increasing temperature, can be attributed to the conductivity relaxation.

To explain the temperature independent dielectric strength, a model has been proposed by Yamamoto and co-worker [17]. Yamamoto and co-worker concluded that the polarization mechanism is associated with the accumulation of charges at the interface between regions of different conductivity. The low frequency behavior of $\varepsilon'(\omega)$ can be explained by Koops's [18] theory which is based on Maxwell–Wagner model. In Koops's theory the solid is assumed to be composed of well conducting grains separated by highly resistive thin layers, grain boundaries. When a signal voltage is applied to the sample, due to the voltage drop across