Dielectric properties of Ag/Ru_{0.03}-PVA/*n*-Si structures

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Abstract. Ag/Ru_{0.03}-PVA/*n*-Si structures were successfully prepared and their morphological and electrical properties were investigated. The obtained electrical results suggested that the complex dielectric constant ($\epsilon^* = \epsilon' - j\epsilon''$), complex electric modulus $M^* = M' + jM''$, loss tangent ($\tan \delta$) and alternating current (ac) electrical conductivity (σ_{ac}) are all a strong function of the frequency (f) and applied voltage. The changes in these parameters are the results of the existence of the surface states (N_{ss}) or interface traps ($D_{it} = N_{ss}$), interfacial polymer layer, surface and dipole polarizations and hopping mechanisms. The values of ϵ' and ϵ'' show a steep decline with increasing frequency and then reach a constant value at high frequency, whereas the increments of M' and M'' with frequency are exponential. The $\tan \delta$ vs. $\log f$ plot has a strong peak behaviour, especially in the accumulation region. These experimental results suggested that the Ru_{0.03}-PVA interfacial layer could be used as a high dielectric material instead of conventional materials.

Keywords. Ag/Ru_{0.03}-PVA/*n*-Si; impedance spectroscopy; frequency dependence; surface states.

1. Introduction

In recent years, metal-polymer-semiconducting (MPS) structures have been preferred to metal-insulator/oxide-semiconductor (MIS or MOS) structures because using a polymer interface layer with a doped and un-doped material between the metal and semiconductor is a very simple, inexpensive, flexible and effective method for energy consumption. An organic film/polymer establishes a physical barrier at the metal-semiconductor (M/S) interface. In particular, high dielectric materials can hinder the inter-diffusion in the M/S interface and alleviate the reduction of the electric field (E) in MIS, MOS and MPS type electronic devices [1–9].

The quality and reliability of these devices depend on parameters such as the interfacial layer thickness (homogeneity/rate of doping metal), barrier formation and the height of the barrier at the M/S interface, sample or surface preparation and surface states (N_{ss}) and their relaxation times (τ). On the other hand, the series resistance (R_s), concentration of doping donor or acceptor atoms (N_D or N_A), sample temperature, applied frequency and voltage and polarization processes also affect the performance of the devices [10–13]. Therefore, the dielectric properties of M/S structures can be changed using suitable high-dielectric organic or metal-doped organic materials.

There are various organic materials with dielectric properties such as polyaniline, polypyrrole, polypropylene [14], polyvinyl pyrrolidone [3], polyvinylidene fluoride [15,16] and polyvinyl alcohol (PVA) [3]. Among these materials,

PVA is the best choice because of its wide range of optical transparency spectra and its low-temperature sensitivity [17]. Thus, these features make PVA very suitable for use in electronic devices under different environmental conditions. However, these polymers have poor electrical conductivity, but their conductivity increased slightly *via* doping with metals such as Zn, Co, Ni, Bi, Ru and Cu at different rates [2,3,16]. Among these metals, ruthenium (Ru) is an attractive metal due to its promising characteristics such as low resistivity ($7.1 \mu\Omega$ cm in the bulk), high work function (4.7 eV) and feasibility for the dry etch process [18–20]. These features facilitate using Ru-based thin organic films in semiconductor device applications such as Schottky barrier diodes and capacitors.

Because of surface states and dislocations between the metal and semiconductors, both the dielectric and electric properties of the structure may deviate from the ideal case. In this case, the values of capacitance and conductance may be a strong function of frequency and voltage [12,14,21]. In addition, various polarization mechanisms such as interfacial, dipolar or oriental, atomic and electronic polarizations may be effective in the different frequency ranges. Interfacial and dipolar polarizations are more effective among them, especially at low frequencies, but their contribution to the dielectric properties can be ignored, especially at low frequencies [1,17]. In other words, the diffusion of the doped metal in the polymer matrix plays a significant role in the conduction mechanisms and in the electrical and dielectric properties.

The aim of the present study is the fabrication of the Ag/Ru_{0.03}–PVA/*n*-Si (MPS) structure and the characterization of its dielectric properties by using impedance measurements containing a set of capacitance/conductance–voltage–frequency (C/G – V – f) measurements in the frequency of 500 Hz–5 MHz and the voltage of ± 5 V. In this way, the values of the real and imaginary components of permittivity (ϵ' and ϵ''), loss tangent ($\tan \delta$) and real and imaginary components of the electric modulus (M' and M'') of the fabricated Ag/Ru_{0.03}–PVA/*n*-Si (MPS) structure were obtained from the capacitance and conductance measurement results at room temperature and they were also compared in detail with the available literature.

2. Experimental

Ag/Ru_{0.03}–PVA/*n*-Si structures were fabricated on a P-doped (*n*-type) single crystal Si wafer that had a (100) orientation, a diameter of 5.08 mm, a thickness of 300 μm and a resistivity of 1–10 $\Omega\text{ cm}$. At first, this wafer was cleaned in an ultrasonic bath for five minutes using acetone and isopropyl solutions and then quenched in deionized water with high resistivity (18 M $\Omega\text{ cm}$) for prolonged and sufficient time. A 150 nm-thick Au layer of high purity (99.999%) was coated on the backside of the *n*-Si wafer by using the metal evaporation system at a pressure of about 4×10^{-6} Torr. Then this wafer was annealed at 550°C for 3 min in a dry N₂ atmosphere in order to obtain good ohmic contact. After the formation of the ohmic contact, the coating on the backside of the wafer was cleaned for 5 min using an HF + 10H₂O ultrasonic bath to prevent possible native oxidation on the front side of the Si wafer. Finally, it was rinsed with deionized water with high resistivity for 30 s and was dried by N₂.

Ruthenium (III 24%-minimum) and PVA (MW~40,000) were purchased from Alfa-Aesar. Ethanol was used as the solvent in this study. First, a PVA solution (10 w:w) was prepared *via* dissolving the PVA in water by stirring for 2 h at 80°C. An appropriate amount of ruthenium (Ru) was added to the PVA solution to obtain the 0.03 molar ratio of Ru in PVA. The solution was stirred for 2 h at 60°C using a magnetic stirrer to obtain a clear and homogeneous solution. The Ru_{0.03}–PVA nanofibre film was made on an *n*-Si wafer *via* the electrospinning technique. Badali *et al* [22] have explained the working conditions of this technique. SEM images of the material were obtained by field emission scanning electron microscopy (GEMINI column ZEISS-SUPRA 40 VP). The diameters of the nanofibres were obtained *via* ImageJ 1.51p software.

To create the rectifier contact area, pure Ag (99.999%) was coated on the Ru_{0.03}–PVA thin film with a contact area of $7.80 \times 10^{-3}\text{ cm}^2$ and a thickness of 150 nm in a high vacuum metal evaporation system with a pressure of about 4×10^{-6} Torr by using a metal shadow mask. Thus, the fabrication process of the MPS structure was completed. The thickness

of the interfacial Ru_{0.03}–PVA layer was estimated to be about 30 nm from the interfacial layer capacitance ($C_i = \epsilon' \epsilon_0 A / d_i$) at a 1 MHz capacitance–voltage (C – V) plot.

3. Results and discussion

SEM images were used to observe the electrospun nanofibres on the Si wafer. These images are shown in figure 1a and b with a zoom-in view of 5000 and 20,000, respectively. As shown in these figures, there is a regular nanofibre formation on the Si wafer. The nanofibres have a flexible and stable structure. The beady structure is not seen in these figures. Therefore, it can be said that the electrospinning process was completed successfully. Figure 1c shows a histogram graphic *via* SEM images. This figure shows that the diameters of the nanofibres are usually measured from 100 to 120 nm. Moreover, the average of the nanofibre diameters was calculated and found as 113.803 nm.

The dielectric properties and electric modulus formalism of MIS and MPS type diodes and capacitors can be expressed by means of different representations such as a comparison of complex dielectric (ϵ^*) and electric modulus (M^*) in a wide range of frequency and temperature. For this purpose, both the forward and reverse bias impedance measurements of the fabricated Ag/Ru_{0.03}–PVA/*n*-Si structures were carried out in a wide range of frequency (0.5 kHz–5 MHz) and voltage (± 5 V). The values of ϵ' , ϵ'' and $\tan \delta$ were obtained from the measured experimental capacitance (C) and conductance (G/ω) values by using the following expressions [23,24]:

$$\epsilon' = Cd_i/\epsilon_0 A = C/C_0 \quad (1)$$

$$\epsilon'' = Gd_i/\epsilon_0 \omega A = G/\omega C_0 \quad (2)$$

$$\tan \delta = \epsilon''/\epsilon' \quad (3)$$

where d_i is the thickness of the Ru_{0.03}–PVA interlayer, A is the rectifier contact area in cm^2 , ω is the angular frequency and ϵ_0 is the permittivity of vacuum ($\epsilon_0 = 8.85 \times 10^{-14}\text{ F cm}^{-1}$). The voltage dependence of ϵ' , ϵ'' and $\tan \delta$ are shown in figure 2a–c, respectively.

When the MIS/MOS or MPS structures are exposed to the forward or reverse bias voltage, the capacitance–voltage (C – V) or ϵ' – V plots usually have three regions which are called accumulation, depletion and inversion regions [13]. When a negative ($V < 0$) voltage is applied to a metal rectifier contact, the top of the valance band (E_v) bends upward and it is closer to E_F . This band bending causes an accumulation of the majority carriers near the semiconductor surface and this is called the accumulation region. When a small positive voltage ($V > 0$) is applied, the bands bend downward and the majority carriers (electrons in *n*-type and holes in *p*-type) are depleted and this is the depletion region. Finally, when a larger positive voltage ($V > 0$) is applied, the bands bend more downward and in this case the electron concentration (minority carriers) at the surface is larger than that in

Figure 1. The SEM images of nanofibres on the Si wafer: (a) 5000 zoom-in view, (b) 20,000 zoom-in view and (c) histogram of the nanofibre diameters.

the holes. In this case, dipoles are inverted and this is called the inversion region. As seen in figure 2a and b, the voltage ranges of $V < -1$, $-1 < V < 1$ and $V > 1$ correspond to the accumulation, depletion and inversion region, respectively.

In addition, frequency-dependent profiles for ϵ' , ϵ'' and $\tan \delta$ in the accumulation region are shown in the inset of figure 2a–c, respectively. According to these figures, the values of ϵ' , ϵ'' and $\tan \delta$ are strongly dependent on the voltage and frequency. The values of ϵ' and ϵ'' exponentially decrease with increasing frequency due to possible polarization mechanisms (figure 2a and b). The variations of ϵ' and ϵ'' are dependent on various factors such as interfacial layers, dielectric relaxation of polarized dipoles in the structure and interface/surface states and their relaxation time. Both the dipole orientation and interfacial/surface polarization mostly occur at low and intermediate frequencies. Similarly, surface states or traps can follow the alternating signal at low frequencies and yield an excess C or ϵ' . Such behaviour was explained by the Maxwell–Wagner relaxation due to the dipolar and the interfacial polarizations. On the other hand, at high frequencies, interface traps cannot contribute to C and G because the charges at these traps cannot follow the alternating ac

signal. In other words, the decrease in C and G at intermediate frequencies means that only a small part of the interface states can follow the ac signal and at high frequencies ($f \geq 1$ MHz), the contribution of interface states to the C and G can be neglected.

As can be seen in figure 2c, the $\tan \delta$ vs. V curves have a distinct peak at about -0.5 V that depends on the ϵ' and ϵ'' values and its magnitude decreases with increasing frequency. The origin of this peak is usually a result of the particular density distribution of surface states (N_{ss}) at the M/S interface, dipole polarizations and R_s of the device [6]. The position of the peak in the $\tan \delta$ vs. V curve shifts toward the high forward bias with decreasing frequency under an external electric field, which records and restructures charges at surface states [25–27]. Moreover, such behaviour of $\tan \delta$ with frequency can be attributed to the hopping mechanism in the externally applied field. In figure 2c, the $\tan \delta$ vs. $\ln f$ curve in a strong accumulation region also shows peak behaviour.

The analysis of the electric modulus, via the impedance spectroscopy method, which contains a set of capacitance–voltage ($C-V$) and conductance–voltage ($G/\omega-V$) curves as a function of frequency can supply more information on

Figure 2. The voltage-dependent plots of the Ag/Ru_{0.03}-PVA/n-Si structure for various frequencies: (a) ϵ' , (b) ϵ'' and (c) $\tan \delta$.

the relaxation process in materials. The values of M' and M'' were obtained from the experimental values of ϵ' and ϵ'' data by the following equation [23,24,28,29]:

$$M^* = 1/\epsilon^* = M' + jM''$$

$$= \frac{\epsilon'}{(\epsilon')^2 + (\epsilon'')^2} + j \frac{\epsilon''}{(\epsilon')^2 + (\epsilon'')^2}. \quad (4)$$

Figure 3a and b displays the M' vs. V and M'' vs. V curves between 0.5 kHz and 5 MHz for the Ag/Ru_{0.03}-PVA/n-Si structure. In these figures, the M' value is almost increased with increasing voltage in both depletion and accumulation regions, whereas the M'' vs. V curve shows a peak behaviour at low frequencies. As can be seen from these figures, the increments of M' and M'' with frequency are exponential. However, the change is slightly different in the low, middle and high frequencies. These changes of M' and M'' with frequency can generally be attributed to the specific distribution of the interface states located between the interfacial

organic layer and n -Si in the forbidden bandgap of Si and their relaxation/life time. The changes in M' and M'' with frequency and voltage can be explained using the Debye theory [8]. According to this theory, for lower frequencies, the value of τ is lower than the period ($T = 1/f$). In this case, dipoles can follow the external ac signal. As shown in figure 3a and b, M' and M'' reached a maximum value at high frequency due to the relaxation process ($M_\infty = 1/\epsilon_\infty$) [1,13].

The frequency-dependent dielectric properties show two relaxation processes: (1) the Maxwell-Wagner relaxation process at low frequencies and (2) the ionic conduction relaxation process at middle frequencies. The alternating ac conduction and electric modulus studies support the hopping type of conduction in the composites. Figure 4 shows that the conduction is a function of frequency and it increases with increasing frequency. The ac conduction is the result of localized surface states in the interfacial layer and can be expressed using Joncher's power law [30,31].

Figure 3. The voltage-dependent plots of the Ag/Ru_{0.03}–PVA/n-Si structure for various frequencies at room temperature: (a) M' and (b) M'' .

Figure 4. The voltage-dependent σ_{ac} vs. V plots of the Ag/Ru_{0.03}–PVA/n-Si structure for various frequencies at room temperature.

$$\sigma_{ac} = (d/A)\omega C \tan \delta = \varepsilon'' \omega \varepsilon_0 = \sigma_{dc} + A\omega^s \quad (5)$$

where σ_{ac} and σ_{dc} are the ac and zero frequency direct current (dc) conductivity, ω is the angular frequency, A is a pre-exponential constant, which determines the strength of polarizability, and s is a power-law exponent according to Funke [32]. Both A and s are weakly dependent on temperature. According to Jonscher, all materials should follow the power law according to a $0 < s < 1$ factor. It means that the hopping motion involves a translational motion with a sudden hopping. Nowadays, some materials have shown n factors above 1, which means the motion involves localized hopping without the species leaving the neighbours [33].

In figure 4, at low frequency, the value of σ_{ac} is almost unchanged with a frequency that corresponds to dc conductivity. Furthermore, at high frequency, it increases with increasing frequency, corresponding to ac conductivity.

Considering the above discussion, the (Ru_{0.03}–PVA) interfacial layer can be used as a high dielectric material instead of conventional low dielectric materials such as SiO₂ and SnO₂. Thus, it can be used in the fabrication of high dielectric capacitors capable of saving more energy. Such a high dielectric interfacial layer can also increase the performance of the MS structure especially with respect to decrease the magnitude of N_{ss} , R_s and barrier inhomogeneity.

4. Conclusion

In this study, the frequency- and voltage-dependence values of ε' , ε'' , $\tan \delta$, M' , M'' and σ of the Ag/Ru_{0.03}–PVA/n-Si (MPS) structure were investigated in a wide range of frequency and voltage. An analysis of the results of these parameters revealed that the interfacial layer, surface states, series resistance and polarization processes have a greater effect on the dielectric properties that should be taken into account for determining dielectric properties. The obtained high values of ε' and ε'' especially at low frequencies ($f \leq 10$ kHz) can be attributed to the conductivity directly related to the increase in the mobility of charge carriers at traps or states and the Maxwell–Wagner polarization mechanism. The obtained experimental values of M' and M'' for various applied bias voltages increase with increasing frequency and they reach a maximum value at 5 MHz. The effect of N_{ss} and polarization decrease with increasing frequency because of the charges at traps and dipole cannot follow the ac signal due to low

values of the relaxation time. Such behaviour of these plots confirmed that the conduction behaviour at the low and high frequency is considerably different in the Ag/Ru_{0.03}–PVA/*n*-Si structure. It can be deduced that the Ru_{0.03}–PVA interfacial layer can be used as a high dielectric material instead of conventional materials with low dielectric constants such as SiO₂ and SnO₂. Thus, the Ru_{0.03}–PVA interfacial layer can be used for the fabrication of high dielectric capacitors capable of storing more energy.

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