



Investigation of frequency and voltage dependence surface states and series resistance profiles using admittance measurements in Al/p-Si with Co₃O₄-PVA interlayer structures



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ABSTRACT

Al/Co₃O₄-PVA/p-Si structures were fabricated, and their surface states (N_{ss}) and series resistance (R_s) profiles were obtained using admittance technique in the frequency range of 5 kHz–1 MHz at room temperature. The values of both capacitance (C) and conductance (G/ω) decrease with increasing frequency due to the existence of N_{ss} , interfacial layer and surface polarization. The G/ω - V profile has two distinctive peaks for each frequency at about 0.9 V and 1.5 V due to the particular density distribution of N_{ss} at p-Si/Co₃O₄ interface, interfacial layer and R_s of the structure. The magnitude of two peaks increases with decreasing frequency and shift towards negative voltages. N_{ss} - $\ln(f)$ profile that obtained from Hill Coleman technique decreases exponentially with increasing frequency. Voltage dependent profile of R_s was obtained from C and G/ω data using Nicollian and Brews technique. It has two peaks and peak values decreases with increasing frequency. In addition, the concentration of acceptor atoms (N_A), Fermi energy level (E_F) and barrier height (BH) values were obtained from reverse bias C^{-2} - V plots for each frequency at room temperature.

1. Introduction

The metal-insulator/polymer-semiconductor (MIS or MPS) type structures are significant devices in semiconductor optoelectronic technologies. As can be seen in many studies in recent years, the conduction mechanism and formation of BH at M/S interface could be changed by using an appropriate interlayer between semiconductor and metal [1]. Nano structures are constructed at sizes in the range of 1–100 nm, as can be understood from the definition of structures [2–4]. It is very useful for humankind that nano-sized structures can be produced in different sizes, shapes and combinations. In many areas of technological applications such as nano-electronics, biological and medical detection, data processing, they are actively used. Metal oxide nanostructures are one of the most popular nanostructures. [5]. Cobalt oxide (CoO), as an important metal oxide, is a promising transition metal oxide material. It is an important p-type semiconductor, and five species of them have been reported (CoO₂, Co₂O₃, CoO(OH), Co₃O₄ and CoO). However, cobalt oxide with valence of more than three is unstable in the natural environment. Other cobalt oxides (Co₃O₄ and CoO) are more stable and useful in industry. At the same time, Cobalt oxyhydroxide, CoO(OH), a divalent metal cation, has a hexagonal

structure in an octahedral site coordinated with six hydroxyl oxygen [6]. Cobalt oxide is widely used in such fields as superconductivity [7], electrochromic [8], Li-ion battery devices [9], catalysts [10], pigments [11] and solid state sensors [12].

Metal semiconductor (MS) contacts, known as Schottky barrier diodes (SBDs), are a special diode type with very low forward voltage drop and very fast switching characteristics. In today's technology, MS contact based devices such as solar cells and photodiodes have a very important place [13]. MS type SBDs are converted to MPS type SBDs by an interface polymer layer. MPS structure is the most appropriate to prove the relevance between the insulator and semiconductor layers. For this purpose, a Co₃O₄-doped PVA interface layer was formed on the p-Si wafer by electrospinning method to improve the electrical performance of the Al/p-Si (MS) type SBD. Over the centuries, the use of pure or metal-doped polymers, graphene or graphene oxide (GO) and metal oxide nanostructures as interface isolators between metals and semiconductors in science and technology has attracted considerable attention [14–19]. There are many methods to detect the density distribution of N_{ss} and R_s [20,21]. The best well known of them are the low-high frequency capacitance (C_{LF} - C_{HF}), Hill Coleman and Nicollian and Brews techniques, respectively [20–22]. While the effect of N_{ss} and

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interfacial layer are more effective especially at low frequencies in the inversion and depletion regions, R_s is effective at high frequencies at only strong accumulation region. It is well known, the performance of these diodes is effected by frequency and applied bias voltage, series R_s and N_{ss} , doping concentration of donor or acceptor atoms, the thickness and homogeneity of interfacial layer, surface processing, BH between metal and semiconductor. In addition, the existence of an interfacial layer at metal/semiconductor (M/S) interface and N_{ss} lead to deviation from the linearity in C^{-2} -V plot. In order to see the effect of these parameters on C-V and G/ω -V characteristics, they were calculated by using Nicollian and Brews, Hill Coleman and the high-low frequency capacitance techniques, respectively [20–24].

In our previous study, impedance spectroscopy methods (C-V and G/ω -V) at room temperature were used to investigate the frequency and voltage dependence of the dielectric properties of Al/Co₃O₄-PVA/p-Si structures. Experimental results obtained from a wide range of frequency and voltage showed that Co₃O₄ doped-PVA interface layer, N_{ss} polarization and the applied bias voltage are very effective in dielectric properties and conductivity. The purpose of this study is to investigate the changes in R_s and N_{ss} of these structures with frequency and voltage at room temperature. Some important electrical parameters such as the Fermi energy (E_F) and the barrier height (Φ_B (C-V)) were calculated from the linear parts of the reverse polarization (C^{-2} vs V) curves for each frequency using acceptor atoms (N_A).

2. Experimental procedures

Al/Co₃O₄-PVA/p-Si structures were fabricated on (p-Si) single Si wafers with (100) orientation, ~300 μm thickness and 1–10 Ω cm resistivity. First, the p-Si wafer was cleaned at 55 °C acetone for 10 min, immersed in methanol and quenched in deionized (DI) water. Second, the p-Si wafer was etched in a solution of H₂O, NH₄OH and H₂O₂ (65:13:13 v/v) at 70 °C and then etched in a H₂O: HF (24:1 v/v) solution. Finally, p-Si wafer was dried in the dry nitrogen (N₂) gas. After cleaning processes, p-Si wafer immediately was transferred into the deposition chamber. High purity (99.999%) Al with a thickness of 1500 Å was thermally evaporated on the entire backside of the p-Si wafer at a pressure of ~10⁻⁶ Torr and the wafer was heated to 500 °C in a nitrogen atmosphere and then it was annealed to achieve a good ohmic contact. In order to increase the quality of Al/p-Si (MS) structure, Co₃O₄-PVA composite prepared on p-Si wafers was added to the front surface in the metal evaporation system in high purity, 1 mm diameter (7.85×10⁻³ cm⁻²) and Al points of 1500 Å thick were amplified and then precipitated. After these steps, the fabrication of Al/Co₃O₄-PVA/p-Si structures has been completed. To perform the C-V and G/ω -V measurements, the samples were glued onto the Cu holder with the help of silver paste and the upper Schottky contacts were tied with silver paste and fine Cu wires. The electrical measurement system was given in Fig. 1. Impedance measurements were performed in a VPF-475 cryostat to further reduce external effects and noise with a HP-4192A LF impedance analyzer and a microcomputer and an IEEE-488 AC/DC converter card. More detailed information on the production process, structural and optical analysis and schematic diagram of the structure is available in our previous work [17].

3. Results and discussion

It is well known, in ideal case, the value of C of the MS and MIS type SBDs depends on usually applied voltage, not on frequency. However, this situation may be considerably different in applications. Figs. 2 and 3 show the C-V and G/ω -V characteristics of the Al/Co₃O₄-PVA/p-Si structures in the frequency range of 5 kHz–1 MHz, respectively.

As can be seen Figs. 2 and 3, the values of both C and G/ω are considerably depend on the frequency and applied bias voltage. The changes in C and G/ω are quite high especially in depletion and accumulation regions at low frequencies due to the existence of N_{ss} and

R_s . Such behavior of C and G/ω in the accumulation region is the result of the ability of charges at states/traps to follow the external ac signal. The G/ω -V curve has two clear distinctive peaks, which are corresponding to the depletion and accumulation regions for each frequency at about 0.9 V and 1.5 V, respectively. The first peak in the depletion region can be attributed to the particular density distribution of N_{ss} and surface polarization, but the second peak in the accumulation region can be attributed to the existence of R_s and interfacial layer [25]. In general, the deviations of the C-V and G/ω -V characteristics from the ideal behavior are resulting from the various sources such as interfacial layer and its homogeneity, the existence R_s , the charges at traps and their relaxation times (τ), barrier inhomogeneity at M/S interface, doping concentration level, polarization, frequency and sample temperature. While the magnitude of peak in the forward bias G/ω -V plot decreases with increases frequency, its position shift towards the positive biases due to special distribution of N_{ss} at M/S interface and reordering and restructure of them under electric field. It is well known that at low frequency, the charges at traps can easily follow the ac signal. Thus, they yield an excess capacitance and conductance to the measured C and G/ω values [15,20,26,27]. On the other hand, at sufficiently high frequencies ($\omega\tau \geq 1$) the charges at traps cannot follow the ac signal, so that they cannot yield an excess capacitance ($C_{ex.}$) and excess conductance ($G_{ex.}$) to the measured C and G/ω values.

The existence of R_s in the electronic device can cause serious errors in the extraction of electrical parameters from admittance measurements. In order to see the effect of R_s on the C-V and G/ω -V plots of the structure, the voltage dependent resistance (R_i) of the sample was extracted from the measured C and G data by using the Nicollian and Brews method [20] for each frequency. According to this method, the real value of R_s can be obtained from the measured C and G values at strong accumulation region for sufficiently high frequencies ($f \geq 500$ kHz) by using following equation;

$$R_i = \frac{G_{ma}}{G_{ma}^2 + (\omega C_{ma})^2} \quad (1)$$

where, C_{ma} and G_{ma} are the measured values of C and G at strong accumulation region. Using the measured C and G for any applied bias voltage at each frequency, Eq. (1) can also be used for the extraction of voltage dependent profile of the R_i . The R_i -V plot for each frequency is given in Fig. 4. This is very significant to give attention to the effect on the value of R_i in the applications of the frequency and voltage dependence of the C and G measurements. As can be seen in Fig. 4, the value of R_i is strongly dependent on frequency and applied bias voltage especially in the depletion and accumulation regions. The value of R_i at strong accumulation region is corresponding to the real value of R_s at higher frequencies and it decreases with increasing frequency as expected. On the other hand, the R_i -V plot has two distinctive peaks at about 0.9 V and 1.5 V. The magnitude of the peaks decrease with increasing frequency and their positions shift towards to negative bias voltage like to G/ω -V plots due to reordering and restructuring of carrier charges in the traps under applied bias voltage or electric field effect [28].

In MS and MIS or MPS type SBDs structures, the depletion layer capacitance can be expressed as [15].

$$C = \left[\left(\frac{q\epsilon_s\epsilon_0 N_A A^2}{2} \right) \left(V_{bi} - \frac{kT}{q} - V_R \right) \right]^{\frac{1}{2}} \quad (2)$$

Thus, some main electrical parameters such as V_{bi} , E_F and Φ_B (C-V) can be extracted from the linear parts of C^{-2} -V plots for each frequency by using Eq. (3).

$$C^{-2} = \frac{2(V_{bi} - kT/q - V)}{q\epsilon_s\epsilon_0 A^2 N_A} \quad (3)$$

where, V_{bi} is the build-in voltage corresponding to intercept voltage, V is the applied bias voltage, ϵ_0 is the dielectric constant of free space

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