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WORK FUNCTION ESTIMATION OF BISMUTH DOPED ZNO THIN FILM

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ABSTRACT

In this paper we report bismuth (Bi) doped ZnO based heterojunction devices. The p-type Bi doped ZnO thin films have been deposited on n and p type silicon substrate using sol-gel spin coating method. The p-type nature of the deposited Bi doped ZnO thin films have been analyzed by hot point probe method. The electrical properties of the fabricated devices have been obtained from I-V characteristic measured using semiconductor parameter analyzer. Finally, the work function of Bi doped ZnO has been estimated from the electrical parameter obtained from I-V calculations.

KEYWORDS

Bi doped ZnO, P type ZnO, Sol-Gel, Work Function

1. INTRODUCTION

Innovative thinking and continuous modification have lead to the development of new generation of semiconductor devices. As far as the future of the semiconductor devices is concerned, ZnO has a major role to play in it as it is versatile and has interesting properties like resistivity control over the range of 10^{-3}–10^{-5} Ω-cm, transparency in the visible range, high electrochemical stability, direct band gap (3.3 eV), absence of toxicity and abundance in nature [1-2]. Therefore, it can be stated that versatility of ZnO ranges from optical, electrical, piezoelectricity, ferromagnetic to gas sensing properties [3-5]. Further, large binding energy of 60 meV as compared to 25 meV of GaN makes ZnO technically efficient approving it for the field of optoelectronic applications. Thin films of ZnO can be used as a window layer and also as one of the electrodes in optoelectronic devices such as solar cells [6]. Along with this application, ZnO thin films have been used in varistors, gas sensors, solar cell transparent contact fabrication, etc [7-9]. It is worth mention here that requirement of an optoelectronic device is good quality p-doped ZnO, and p-n junction, but developing a good quality p-doped ZnO is quite challenging because of its instability at room temperature [10-12]. Growth of p-type ZnO has been thought of in various ways including substitution of elements from Group IA or II B of periodic table on a Zn site, substitution of elements from Group VA on the O site, and codoping with donors and acceptors [13-15]. Bi is one of the important dopant to make ZnO p-type and is post-transition element that lies to the right of transition metals and to the left of the metalloids [16-17]. Bi doped ZnO leads to faster carrier migration. In this connection, using to the several attractive properties of Bi doped ZnO we have previously analyzed influence of Bi concentration in ZnO in terms of nature, structural and optical properties [18]. Further, using as the as obtained p-type Bi doped ZnO thin film we have reported the fabrication of Au based schottky diode [16]. Now, in the present paper p-type Bi doped ZnO/p-Si and p-type Bi doped ZnO/n-Si heterojunctions have been fabricated and work function of the ZnO film was estimated using the calculated electrical parameters of I-V characteristics.

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2. EXPERIMENTAL DETAIL

2.1. Cleaning of Silicon Wafer

The p-type and n-type Si <100> substrates have been cleaned using RCA-1 and RCA-2 method to eliminate organic and ionic impurities from the surface before the films deposition. The RCA-1 solution is the combination of DI water, NH_4OH and H_2O_2 in the proportion of 5:1:1, and the RCA-2 solution is combination of DI water, HCL and H_2O_2 in the proportion of 6:1:1. To clean the samples they were dipped into RCA-1 and RCA-2 solutions separately for 10 minutes at 80^0C then cleaned with DI water. Further, to remove the residual oxide from the surface of the substrate sample, the samples were cleaned with buffered HF solution.

2.2. Deposition of Bismuth Doped ZnO Thin Film

The Bismuth doped ZnO sol of concentration 0.7 M have been prepared using precursor zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$), isopropanol (solvent) and stabilizing agent diethanolamine (DEA). The molar proportion of zinc acetate dehydrates and stabilizer DEA was kept at 1:1. For Bismuth doping we add 10 molar percentage of Bismuth nitrate pentahydrate ($Bi(N0_3).5H_2O$ to the starting solution. The prepared solution was stirred at 60°C for 1 hour and then the prepared sol was reserved for at least 24 hours at room temperature for ageing. Further, Bi doped ZnO thin films have been deposited over n-type and p-type Si substrate by spin coating method. The films have been prepared at spinning speed of 2000 rpm for 20 seconds, and prebaked at 100°C for 10 minutes in oven to evaporate the solvent and organic residuals. The deposition process has been repeated many times to obtain the required film thickness and finally the deposited films are placed in a furnace at 500^0C for 1 hrs with air ambient to improve the crystallization. A 250 nm thick aluminum circular dots have been deposited on the top of ZnO thin films and bottom of Si substrates using thermal evaporation method as shown in Fig.1. For the electrical characterization, I-V plot has been plotted using a semiconductor device parameter analyzer under dark condition.

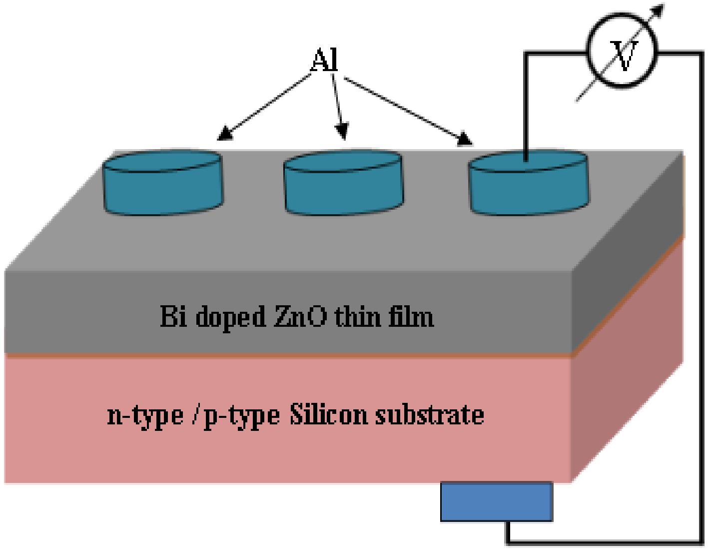

Figure 1. Schematic view of the Bi doped ZnO on p-Si and n-Si heterojunction.

3. RESULT AND DISCUSSION

To determine the nature of majority carriers in the deposited Bi doped zinc oxide thin films a very simple and efficient hot point probe method based on seebeck effect has been performed. From the results, it can be clearly seen that ZnO films doped with Bi shows p- type nature. To confirm the consistency of p-type nature of Bi doped ZnO thin films, the experiment was repeated several time under same experimental condition and subsequently it have been found that outcome remains the same. The typical resistivity of the doped film as observed from hall measurement has been found to be nearly equal to 4.1Ω-cm.

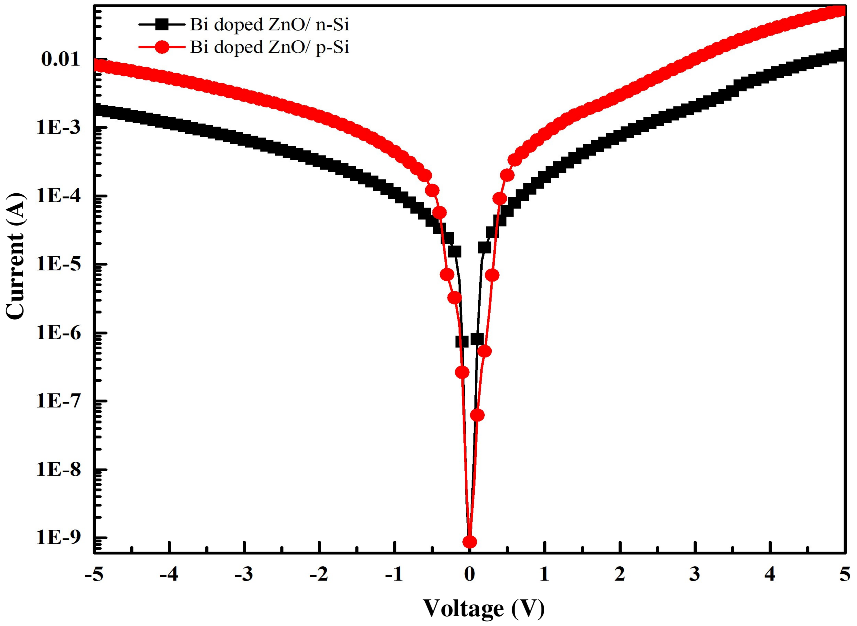

Figure 2. Current (I)-Voltage (V) characteristic Bi doped ZnO/p-Si and Bi doped ZnO/n-Si heterojunction

The I-V characteristic of the deposited heterojunctions have been analyzed using microprobe station and semiconductor device parameter analyzer. The semi-logarithmic I- V characteristics of p-type Bi doped ZnO/p-Si and p-type Bi doped ZnO/n-Si heterojunctions at room temperature for the voltage range between -5V to 5V, have been shown in Fig. 2. From the fig.2 it is clearly observed that the fabricated heterojunctions shows good rectifying characteristics. In the p-ZnO/ n-si heterojunction, Si substrate is connected to the negative terminal of the bias source for forward biasing, while in p-ZnO/ p-Si heterojunction, Si substrate is connected to the positive terminal of the bias source for forward biasing because carrier concentration of silicon is higher than Bi doped ZnO. The fabricated heterojunction shows forward biasing condition which is similar to Schottky junction. We have calculated the reverse saturation current (I_o) by the intercept of straight line portion of ln(I) versus V plot extrapolated for voltages larger than a few KT/q with the zero voltage axis which is then used to estimate the value of barrier height ϕ_B. Further, the result shows very good conductivity of the films therefore it has been implicit that the Fermi level might be very closed to the valence band of doped ZnO. The relation between current and voltage for the fabricated heterojunctions can be given as: [19]

$$I = I_0\left(e^{\frac{qV}{\eta kT}} - 1\right) \tag{1}$$

where q is charge on electron, η is the ideality factor, T is the temperature in Kelvin, K is Boltzmann constant, V is voltage across the junction and I_O is reverse saturation current.The reverse saturation current can be expressed as follow:

$$I_0 = AA^{*}T^{2}e^{-q\varphi_B/kT} \qquad (2)$$

where A is junction area (A=0.515x10^{-2} cm^2), A^* is the effective Richardson constant (A^* =32×10^4 Am^{-2} K^{-2}) for ZnO [20] .The effective barrier height ϕ_B in Eq. (2) can be calculated by using the following equation:

$$\Phi_B = -\frac{kT}{q}\ln\left(\frac{I_0}{AA^{*}T^{2}}\right) \qquad (3)$$

From fig.2 the calculated value of reverse saturation currents (I_o) is 1.5x10^{-7} Amp for p-ZnO/n-Si heterojunction and 3.3x10^{-8} Amp for p-ZnO/p-Si heterojunction. Further, using calculated values of reverse saturation current and equation (3) the effective barrier height has been obtained as Φ_{bn} = 0.71 eV for p-ZnO/n-Si and Φ_{bp} = 0.75 eV for p-ZnO/p-Si heterojunction. The work function of ZnO has been calculated based on the Schottky Mott model using following relations for heterojunctions with n-Si and p- Si substrate respectively.

$$\Phi_m = X_{si} + \Phi_{bn} \qquad (4)$$

And

$$\Phi_m = E_g + X_{si} - \Phi_{bp} \qquad (5)$$

where E_g and X_{si} are the bandgap energy and electron affinity of silicon having values 1.12 eV and 4.06 eV [21]. The calculated value of the work functions for p-ZnO/p-Si and p-ZnO/n-Si heterojunctions are 4.43 and 4.77 eV respectively, which closely matched with work function of defect free ZnO single crystal [21] . Since during the cleaning process of silicon wafer a very thin (~2nm) nonflexible insulating silicon oxide layer has been formed on the surface of silicon which tailored the barrier height. So, the barrier height with insulating SiO_2 layer can be evaluated using Bardeen model which is given by [21].

$$\Phi_{bn} = C(\Phi_m - X_{si}) + (1-c)(E_g - \Phi_0), \text{ for n-Si wafer} \qquad (6)$$

$$\Phi_{bp} = C(E_g - \Phi_m + X_{si}) + (1-c)(\Phi_0), \text{ for p-Si wafer} \qquad (7)$$

Where,

$$C = \frac{\varepsilon_i}{\varepsilon_i + q^2\delta D_s}$$

and δ is the thickness of SiO_2 layer , D_s is density of states and ε_i is total permittivity, ϕ_o is the neutral Fermi level. For a given interfacial layer thickness, (ϕ_{bP} + ϕ_{bn}) =E_g, due to the similarity of the surface state in p and n type Si. Using the values of qD_s=2 x 10^{12}/cm^3 for n-si wafer, δ=1.5nm and ε_i =3.9, ϕ_o =0.27 eV from the work reported by Turner et al. [22] for metal/n-Si Schottky barrier and the work function of ZnO as calculated in this experiment by equation (3) the value of ϕ_{bn} has been evaluated using equation (6) and has been obtained as 0.76eV. Similarly, using the values of qD_s= 3 x 10^{12}/cm^3 for p-Si wafer, and ϕ_o = 0.33 eV from the work reported by Smith et al. [23], ϕ_{bp} has been calculated using equation (7) obtained as 0.72 eV. Further, due to the presence of thin SiO_2 layer between silicon wafer and ZnO film it is observed that ϕ_{bP} decreases and ϕ_{bn} increases as compared to the Schottky Mott model approach. The high temperature deposition of film increases the rate of oxide formation on the surface of silicon hence reducing the density of state which decreases the value of ϕ_{bP} for p-Si device and increases the value of ϕ_{bn} for n-Si devices. The variation in barrier height with temperature may be due to the fact that at high temperature more oxygen diffuses toward Si interface which makes ZnO less stoichiometric by which oxygen induced defects in ZnO decreases the work function of ZnO which in due course decreases the barrier height.

4. CONCLUSIONS

In this paper, Bi doped p-ZnO thin films have been deposited on pSi and nSi substrate using sol-gel spin coating technique. The work function of bismuth doped ZnO thin film have been obtained from the electrical properties of p-ZnO/ p-Si and p-ZnO/ n-Si heterojunctions. The calculated value of the work function based on the Schottky barrier model exhibits value between 4.5 and 4.78 eV for the films. The effect of very thin layer of SiO_2 at the interface of ZnO and Si wafer on the variation of barrier height, have also been analyzed.

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