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Electrical and photovoltaic properties of cobalt doped zinc oxide nanofiber/n-silicon diode

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ABSTRACT

Nanofiber Co-doped ZnO (ZnO:Co) film was deposited on n-type silicon substrate at room temperature by using sol–gel method. Scanning electron microscopy results indicate that cobalt doped zinc oxide film has a nanofiber structure. The electrical and photovoltaic properties of the Au/ZnO:Co/n-Si diode were investigated by current–voltage, capacitance–voltage, transient current and steady state photoconductivity measurements. The Au/ZnO:Co/n-Si diode exhibits a photovoltaic behavior with a maximum open circuit voltage V_{oc} (0.195 V) and short-circuit current I_{sc} (2.63 μA) values under 100 mW cm^2 illumination intensity and the photoconductivity mechanism of the diode is controlled by the presence of continuous distribution of traps. The interface state density for the diode was determined by conductance method under dark and illumination conditions. The interface state density D_{it} and time constant τ values for the diode under dark and 100 mW/cm^2 conditions were found to be 1.26×10^{10} eV^{-1} cm^{-2}, 6.02×10^{-5} s and 9.81×10^{10} eV^{-1} cm^{-2}, 7.35×10^{-7} s, respectively. The obtained photovoltaic and photocapacitance results indicate that the diode can be used both as a photodiode and photocapacitive sensor for visible light sensor applications.

1. Introduction

Zinc oxide (ZnO) is a direct wide band-gap (E_g = 3.37 eV) semiconductor with a large exciton binding energy (60 meV) and it is currently attracting worldwide intense interests because of its importance in fundamental studies and its numerous applications especially as optoelectronic materials [1,2]. It has also attracted significant attention as an efficient material for applications in UV light-emitting diodes, laser diodes, varistors and transparent conducting films [3]. It is well known that semiconductor nanocrystals or nanoparticles (NPs) may have superior optical properties than bulk crystals owing to quantum confinement effects [3]. Nanoscale structures have attracted extensive synthetic attention as a result of their novel size-dependent properties [4–6]. Much attention has been focused on the research of nanostructured semiconductor materials due to their novel physical and chemical properties and wide range of potential applications in nanodevices [7]. There are many reports on the synthesis of Co-doped ZnO thin films as diluted magnetic semiconductors due to their application for magneto-electronic and spintronic devices [8–11] and many useful methods have been used to prepare high quality ZnO thin films, such as, magnetron sputtering, metal-organic chemical vapor deposition (MOCVD), pulsed-laser deposition (PLD), molecular beam epitaxy (MBE) and sol–gel process [12,13]. Among these methods, the sol–gel method has some advantages to prepare large area ZnO thin films at low cost and easy technology [14] and also, Sol–gel dip coating is a simple apparatus with low cost and it can be suitable for preparing nanostructure ZnO films for electronic device applications. Furthermore, although there are a lot of works on heterojunctions with ZnO, any report on the nanostructure Co-doped n-ZnO plus n-Si type junction is absent. In present study, Co-doped n-ZnO nanostructure film was growth on n-type substrate by using sol–gel dip coating method. This has the advantage of high quality and well-defined interface between the n-ZnO and n-type silicon substrate [15]. The performance and photoelectrical properties of a Schottky diode are drastically influenced by the interface quality of junction. In the present study, first successful fabrication of Au/nanostructure Co-doped ZnO/n-Si junction was performed with sol–gel dip coating. The obtained results indicate that the sol–gel dip coating method for the preparation of nanostructure ZnO is useful for the fabrication of metal-oxide semiconductor plus n-type silicon diodes.

2. Experimental details

The precursor sols were prepared from zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), 2-metoxyethanol and monoethanolamine (MEA). Cobalt dopant was introduced as 20 at.%. Zinc acetate dehydrate and Co-dopant were firstly dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature. The molar ratio of MEA to metal ions was maintained at 1.0. The

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prepared mixture was stirred using magnetic stirrer for about 30 min to obtain clear homogeneous solution and then sol was kept for aging for 24 h prior to film deposition. In order to fabricate the diode, the semiconductor used in this study was n-type single crystal silicon ⟨1 1 1⟩ with a thickness of 600 μm, and a resistivity of 5–10 Ω-cm, purchased from University Wafers Company. Firstly, n-type single crystal silicon was cleaned. In order to remove the native oxide on surface of n-Si, the wafer was etched by HF and then it was rinsed in deionised water using an ultrasonic bath for 10–15 min and finally was chemically cleaned according to the method based on successive baths of methanol and acetone. The ohmic contact was formed by evaporating Al metal on the back of Si wafer and then, it was annealed at 570 °C for 3 min in N_2 atmosphere. After cleaning process, Co-doped ZnO film was deposited on n-type silicon by sol–gel dip coating method and then, the film was dried at 200 °C for 10 min into a furnace to evaporate the solvent and remove organic residuals. This procedure was repeated ten times. The Co-doped ZnO film was annealed at 450 °C for 1 h in a furnace. After thermal annealing process, Au metal contacts were formed on ZnO:Co film deposited on n-type silicon using PVD-HANDY/2S-TE (Vaksis Company) vacuum thermal evaporation in the pressure of 4.5×10^{-5} Torr and the contacts were formed in the form of circular dots of 2 mm in diameter and 100 nm thickness. The contact area of the diode was found to be 3.14×10^{-2} cm^2. The current–voltage characteristics were performed using a KEITHLEY 2400 sourcemeter. The capacitance–voltage characteristics of the diode were performed using a HIOKI 3532 LCR meter. Photovoltaic measurements were employed using a 200W halogen lamp. The intensity of halogen lamp was varied by changing the voltage across halogen lamp. The intensity of light was measured with a solar power meter (TM-206). Surface morphology was investigated using a JEOL7001 F scanning electron microscopy.

3. Results and discussion

3.1. Morphological and dark current–voltage characteristics of the Au/ZnO:Co/n-Si diode

Fig. 1a and b shows scanning electron micrograph (SEM) images of the nanofiber ZnO:Co film deposited on n-type silicon substrate. As seen in Fig. 1a, the structure of the film is consisted of nanofibers which, are distributed almost homogenously on silicon surface. The diameter of ZnO:Co nanofibers varies along the fibers, as shown in Fig. 1b.

The current–voltage (I–V) characteristics of the Au/ZnO:Co/n-Si diode are shown in Fig. 2 and I–V characteristics of the diode is analyzed by the following relation:

$$I = I_o \exp\left(\frac{qV}{nkT}\right)\left[1 - \exp\left(-\frac{qV}{kT}\right)\right] \quad (1)$$

where V is the applied voltage, n is the ideality factor, k is the Boltzmann constant, T is the temperature and I_o is the reverse saturation current given by the following relation:

$$I_o = AA*T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \quad (2)$$

where A is the diode contact area, A^* is the Richardson constant (∼36 A cm^{-2} K^{-2} for ZnO) [16]. and ϕ_b is the barrier height. The reverse saturation current and ideality factor values of the diode were determined from the intercept and slope of the linear region of forward bias of Fig. 2 and were found to be 9.89 nA and 2.79, respectively. The barrier height of the diode was calculated using the reverse saturation I_o value obtained from Fig. 2 and was found to be 0.76 eV.

The obtained n value of 2.79 suggests that the diode exhibits a non-ideal behavior. This behavior results from the presence of surface states in ZnO, oxide layer on silicon and series resistance. Furthermore, it is evaluated that I–V behavior of the diode is affected by parasitic resistances such as series resistance R_s and shunt resistance R_{sh}. The junction resistance R_d for the diode can be determined using dark current–voltage characteristics by means of $R_d = \partial V/\partial I$ relation and the plot of R_d vs. V was shown in Fig. 3. The R_{sh} value was calculated from the curve of R_d–V and was found to be 1.83×10^6 Ω. An ideal device requires the higher shunt resistance. The shunt resistance plays a dominant role, when the voltage is between −2 and −0.35 V. In base region, the resistance of the diode increases. In high inversion voltage region, the tunneling current

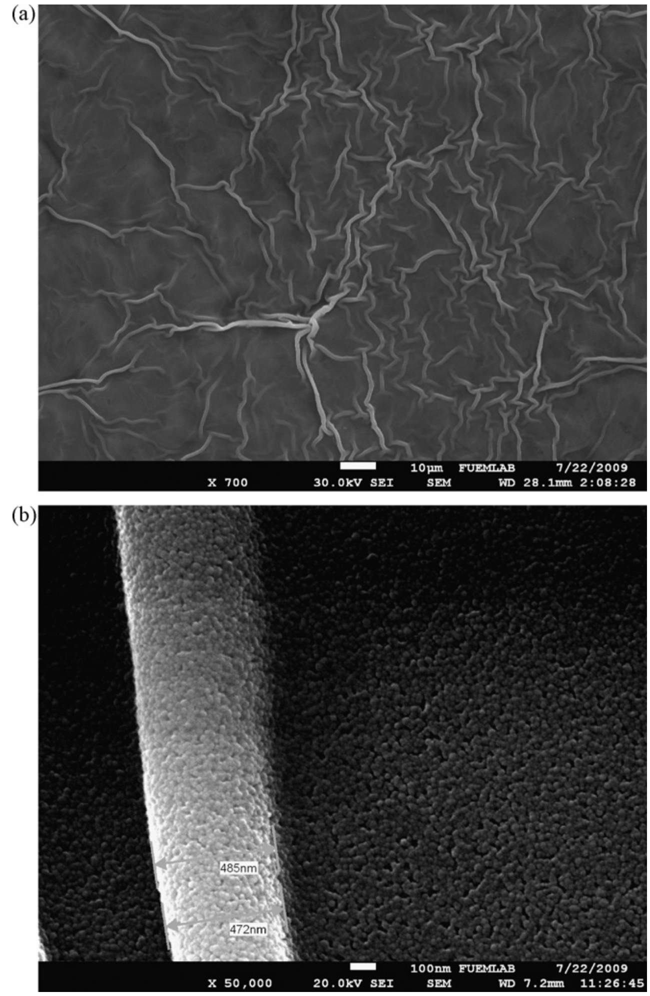

Fig. 1. Scanning electron micrograph images of the nanofiber Co-doped ZnO film.

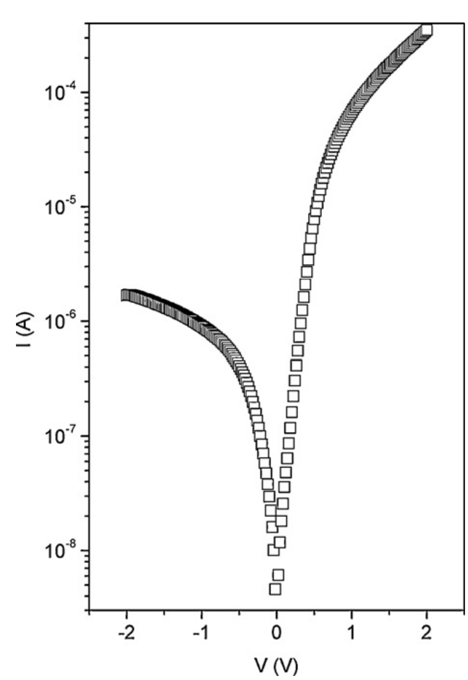

Fig. 2. Current–voltage characteristics of the Au/ZnO:Co/n-Si diode.