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Fabrication and characterization of polyaniline/porous silicon heterojunction

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ABSTRACT

Heterojunction between polyaniline (PANI) and porous silicon (PS) was fabricated by making a layer of PANI on PS, using spin coating method. PS was fabricated by electrochemical etching process. PS was characterized by photoluminescence (PL), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) while the PANI was characterized by FTIR and absorption (UV–VIS) spectroscopy. Current–voltage and capacitance–voltage measurements were done to determine the electrical properties of the heterojunction structure. The ideality factor of the heterojunction was found to be 4.2, which was considered high due to large defect density at the interface. Built-in potential was measured by both *I–V* and *C–V* and was found to be $\Phi_{b(I-V)} = 0.41$ V and $\Phi_{b(C-V)} = 0.28$ V respectively. The discrepancy in the values of the built-in potential was discussed. Band discontinuity in conduction band and valence band were found to be 0.65 and 1.27 eV respectively. Solar response of the heterojunction was also observed at AM (air mass) 1.0 and it showed a promising behavior as a photovoltaic device.

1. Introduction

The electrical conductivity of organic semiconductors has shown great improvement in recent years and as a result very low cost and high performance organic device has been fabricated. During the past decades, intensive research on semiconductor heterostructures has led to the discoveries of many new physical phenomena and device concepts such as semiconductor lasers and photodetectors [1], batteries, LEDs [2], FETs [3], gas sensors [4] and organic solar cells [5]. A new class of heterostructures reported involves contacts between organic and inorganic semiconductors. Several heterojunctions with a thin layer of a molecular semiconductor deposited onto the surface of an inorganic semiconductor substrate such as Si, GaAs, or InP have been found to form rectifiers with characteristics similar to ideal p–n junctions [6]. The main advantages of organic materials include simple and low-temperature thin film processing through inexpensive techniques such as spin coating. One promising approach employs a thin organic film that is layered onto the surface of a conventional inorganic semiconductor substrate to form a hybrid organic/inorganic semiconductor heterojunction device. The main advantage of such hybrid devices is the possibility of altering the composition of the organic film to effect large changes in its optical and electronic properties. Furthermore, different combinations of organic and inorganic semiconductors can be utilized to obtain different desirable properties or applications.

Recently polyaniline (PANI)–silicon (Si) heterojunction has been studied thoroughly. Wang et al. [7] have reported the studies on amorphous Si/PANI heterojunction solar cells. They found open-circuit voltage V_{oc} of the cells ranged from 0.5 to 0.7 V and also illustrated how open-circuit voltages are limited by the work function of the contacting material. Wang and Schiff [5] fabricated heterojunction solar cells using PANI on crystalline Si. They found open-circuit voltage increases with PANI film conductivities. V_{oc} saturated at 0.51 V with increasing PANI conductivity. Dirani et al. [8] fabricated heterojunction diodes using poly (o-methoxyaniline) (POMA)/PANI and amorphous/microcrystalline Si structures. They showed a dependence on the polymer doping level. Laranjeira et al. [9] have reported reliability of Si/PANI heterojunctions on the basis of the degradation effects induced by local heating, charge trapping and temperature changes. The limitation of Si as optoelectronic device is well established due to its indirect bandgap. So, the researchers have been trying to use porous silicon (PS), a highly efficient visible photoluminescence material, which has attracted attention because of its potential application in electroluminescence [10]. A review on the application of porous silicon for electroluminescence was reported by Lang et al. [11]. In that paper they discussed various options for the basic structures based on porous silicon as electroluminescent device. In addition, PANI as a conducting polymer is a good material to make a heterojunction between PS and PANI [12]. PANI has advantage such as its conductivity changes between insulator and metal by doping [13], a conducting layer of PANI can be formed easily and it is stable in air. In heterojunction interface of

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conductive polymer/semiconductor and contact interface of conductive polymer/metal, there is a discontinuity of the conducting mechanism; the conductivity of polymer is explained by a unique mechanism such as soliton, polaron and bipolaron. In the literature, it is observed that heterojunctions based on polyaniline/porous silicon were fabricated mostly for electroluminescent devices and applications. Bsiesy et al. [14] reported fabrication of light emitting diode based on polyaniline/porous silicon and they found emission in the red region on forward biasing it. The authors chemically polymerized polyaniline inside the pores of silicon, whereas Halliday et al. [15] used a solution of polyaniline/camphorsulfonic acid for making a junction directly between the conducting polymer and the porous silicon using a single step process for visible electroluminescence. Matveeva et al. [16], on the other hand, deposited electrically active polyaniline films by electrochemical deposition on porous silicon formed at p- and n-type silicon substrates. The authors noted that deposition of polyaniline was easier on porous silicon formed on n-Si whereas that on p-Si was retarded.

In this paper we have investigated the optical and electrical properties of PS/PANI heterojunction. Due to photoluminescence property of PS and PANI as conducting polymer we made a heterojunction between PS and PANI for photovoltaic application. *I–V* and *C–V* measurements were done to determine the relevant parameters using which the energy band diagram of heterojunction has been drawn to study the conduction mechanism at the interface. Finally, the photovoltaic response was studied.

2. Experimental procedure

PS substrate was obtained by the electrochemical anodization of n-type Si ⟨1 0 0⟩ ($N_D = 10^{16}/cm^3$ and resistivity $\rho = 2.24\,\Omega\,cm$). A typical process for PS preparation is the following: first the Si substrate was cleaned. The wafer was immersed in warm trichloroethylene (TCE) for 5 min and further in acetone for 3 min. Acetone removed the TCE residue and acts as a further cleaning solvent. Then the wafer was immersed in methanol for 3 min. This rinse removes the acetone residue. Finally it was rinsed in deionized water (DI) for 3 min to remove methanol residue. To remove native oxide the wafer was treated with piranha solution having composition H_2SO_4:H_2O_2:H_2O::2:1:1 for 20 min and then it was immersed in DI water to remove any residue. After this, the resulting silicon substrate was electrochemically anodized under a constant current of 30 mA in a HF–ethanol solution (50:50 vol.%) for 30 min. Chemical synthesis of PANI (emeraldine base form) was performed by the same method as described in Ref. [17]. The aqueous solution of aniline hydrochloride (LOBA Chemie, India) and ammonium persulfate (E. Merck, India) was prepared in deionized water (18.2 MΩ). The polymer obtained is the emeraldine salt form of PANI. Emeraldine base (EB)-PANI was prepared from the emeraldine salt by treating it with a concentrated ammonia solution (25%). The precipitate obtained was filtered off, rinsed with distilled water, acetone, and then dried in vacuum. Formation of PANI film on PS was done by spin coating technique. The thickness of the films was ∼1.0 μm.

I–V characteristics of the heterojunction were studied at room temperature using Keithley 2400 source meter. *C–V* measurement was done at 100 KHz using 4249A impedance analyzer.

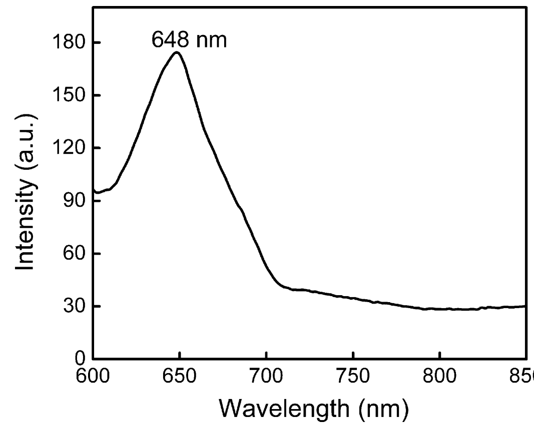

Fig. 1. Photoluminesce spectra of porous Si.

3. Results and discussion

3.1. PL spectrum of PS

PL spectrum of PS was studied by Perkin Elmer (Model LS 55) and is shown in Fig. 1. It was found that the peak emission was at 648 nm. This value of the emission from the PS shows that PS surface is oxidized and also includes the formation of wide-band gap material such as a SiH_x or siloxene [18,19]. From FTIR spectrum it is also observed that Si–O–Si and SiH_x structures exist on the surface of PS.

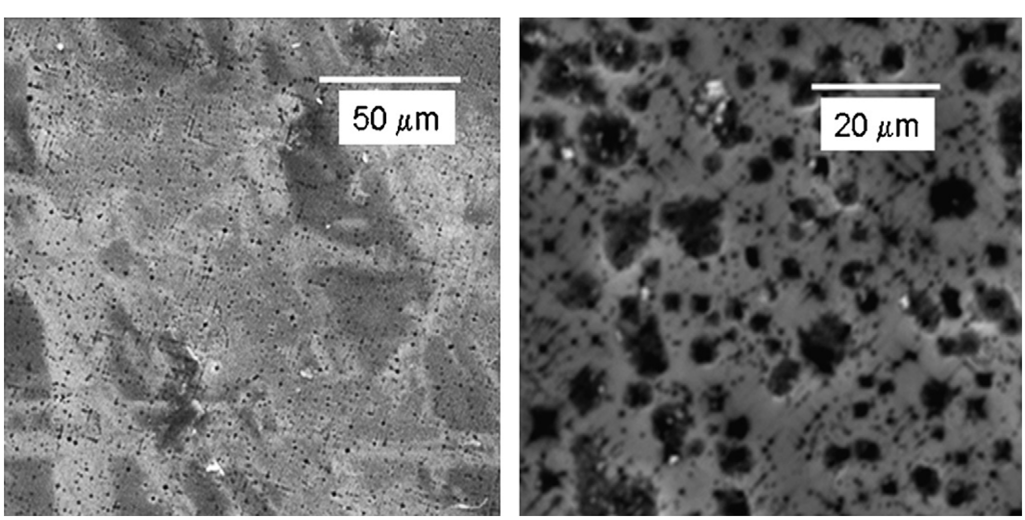

Fig. 2. Scanning electron micrograph of porous Si.