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Fabrication of isotype (p-p) selenium–polyaniline heterojunction diode by electrochemical method

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Abstract

In the present work, for the first time, heterojunction has been fabricated using electrochemically deposited isotype p-selenium–p-polyaniline from a single solution bath. The structural characterization of selenium and polyaniline thin film was carried out using XRD technique. Polyaniline exhibited amorphous structure while selenium offered monoclinic (β) phase. The junction was formed by electrodepositing polyaniline over selenium film and heating at 423 K. The current density versus voltage (*J*–*V*) plot showed the formation of a junction with ideality factor of 1.16. From *J*–*V* characteristics at different temperatures, static resistance (*R*_s), dynamic resistance (*R*_d), and rectification ratio of diodes were determined. Heat treatment above 448 K caused junction breakdown. © 2005 Elsevier B.V. All rights reserved.

Keywords: Heterojunction; Isotype; Junction ideality factor; Selenium; Polyaniline

1. Introduction

Interface formed between two different materials is significant to decide the performance of the devices mostly used for electronic, optical and storage purposes. Formation of type of heterojunction is based on the conductivity of two different materials used and the interface where transition from one material to other takes place. Abrupt anisotype (n-p) heterojunctions are mostly studied interface where transition from one material to other takes place abruptly to change impurity concentration from donor to acceptor. So far in the last thirty years (n-p) anisotype heterojunctions fabricated between inorganic semiconductors employed methods in combination to deposit thin films such as vacuum evaporation, chemical vapour, molecular beam epitaxy, liquid phase epitaxy, vapour phase transport, flash evaporation, sputtering etc. All these methods are highly expensive, time consuming and complicated. The n-p and p-n anisotype heterojunctions such as Ge-Si, Ge-GaAs, Ge-PbS, Si-GaP, Si-PbS, GaP-GaAs, CdS-CdTe, CdS-PbS, CdSe-ZnSe, ZnSe-ZnTe etc. have been studied so far, are minority carrier devices [1]. Recent studies include p-Ag Ga_{0.25}In_{0.75}Se₂–n-CdS junction fabricated by depositing films with flash evaporation and thermal evaporation, respectively, with solar conversion efficiency of 6.3% [2]. Similar to inorganic anisotype heterojunctions, isotype n-n and p-p heterojunctions, which are majority carrier devices, have been fabricated using above methods [3]. Temperature dependent current–voltage (I–V) characteristics of isotype p-Silicon and p-poly-N-epoxipropylcarbazole were studied by Ahmed et al. [4]. Being low cost and having flexible electronic applications, recently much work is going on in devices fabricated using organic polymers with a replacement of metal and inorganic semiconductors [5]. Polyaniline used to fabricate heterojunction, is the most stable conducting polymer that can be easily deposited [6].

The quality of the junction formed between two semiconductors is a consequence of the methods used to fabricate it. Among all physical and chemical methods used to deposit semiconductor thin films, electrodeposition has some advantages. It is easy, economical, low temperature process and particularly suited to fabricate heterojunction solar cell [7]. So far, electrodeposited inorganic heterojunction includes n-CdS– p-CdTe [8], p-CdTe-p-CuInSe₂ [9] etc. Rectifying properties of Schottky diodes were studied by Syed and Saraswathi [10] depositing Au, and In by vacuum evaporation on poly-(*N*methylaniline). In recent years, the formation of solid-state

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Schottky junction between CdS, CdSe and electrodeposited poly-3-methylthiophene has been reported [11–13]. Photovoltaic CuInSe₂–polypyrrole structures were fabricated by Bereznev et al. [14]. Thin film photosensitive junctions between conjugated polymers such as polypyrrole and polythiophene and inorganic CuInSe₂ have been investigated to produce large area photodiode using electrodeposition technique [15].

In electrodeposition, the growth rate of film can be controlled by depositing film in various modes such as, potentiostatic (constant potential), galvanostatic (constant current) or potentiodynamic (varying potential). Electrochemical potentiodynamic mode has advantages over potentiostatic or galvanostatic mode, as the direction of applied potential is reversed at the end of each scan. The scanning of redox electrolyte reversely is useful for probing other species present in the solution. With this aspect of electrochemical potentiodynamic mode, in the present work, by mixing two solutions, the subsequent deposition of selenium and polyaniline films from the same bath has been carried out to fabricate junction between them.

2. Experimental details

2.1. Fabrication of heterojunction

The cross-sectional view of p-Se–p-polyaniline heterostructure is shown in Fig. 1. The heterojunction consists of a electrodeposited layer of selenium deposited on stainless steel substrate over which polyaniline layer is also electrodeposited from the same bath containing aniline and selenium dioxide solution. Front copper contact to polyaniline film and back contact to stainless steel substrate were made to study the junction properties. Details of selenium and polyaniline film junction formation are described below.

An electrolyte solution consist of $0.5 \text{ M H}_2\text{SO}_4$ containing 0.45 M of aniline was used for the polymerization of aniline. The solution was boiled for 15 min, by taking proper care to avoid air oxidation, filtered, cooled and used as a stock solution. A freshly prepared 0.5 M SeO₂ solution was made in double distilled water and 10 cc of monomer aniline solution was mixed with 10 cc of SeO₂ solution. The conventional three electrode cell consisting graphite plate as a counter electrode, saturated calomel electrode (SCE) as a reference electrode was used for deposition. Subsequent depositions of selenium and



Fig. 1. The cross-sectional view of p-Se-p-polyaniline isotype heterostructure.

polyaniline films are carried out using Potentiostat, EG & G Princeton Applied Research Model 263-A with potentiodynamic voltammetry technique in the voltage scan range of -0.7to +2.0 V in a single scan at the scan rate of 50 mV/s. The selenium layer was deposited in the voltage scan of -0.7 to +2.0 V/SCE and over the selenium layer; polyaniline layer was deposited in the voltage scan of +2.0 to -0.7 V/SCE. The p-Se– p-polyaniline heterostructure was air heated at 423 K. For structural analysis, thick films of selenium (thickness 1.2 micron) and polyaniline (1.6 micron) were deposited separately using potentiodynamic technique in above voltage range and studied using XRD technique. For measuring thickness of deposited selenium and polyaniline films conventional weight difference method was used.

Photoelectrochemical study of Se film in 1 M NaOH determined conductivity of Se film as p-type. Thermo-emf measurement determined the type of conductivity of polyaniline as p-type. For this, a small pellet was prepared by scratching powder from the deposited polyaniline film. The contacts between stainless steel and selenium, stainless steel and polyaniline and polyaniline and copper were found to be ohmic -1.5 to +1.5 V,voltage range. The junction p-Se-p-polyaniline was tested for *J*–*V* Characteristics, in voltage range of -1.5 to +1.5 V. Further, the junction was air heated at different temperatures to improve the junction performance.

3. Results and discussion

3.1. Construction and analysis of energy band diagram

For studying the alignment of bands at the interface of p-Sep-polyaniline heterojunction in the present work, the energy band diagram is proposed as in Fig. 2. The equilibrium chemical potentials of selenium and polyaniline films in 1 M KCl solution were separately measured with respect to saturated calomel electrode (SCE). Then the measured



Fig. 2. Energy band diagram of isotype, p-Se-p-polyaniline heterostructure.

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