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Electrical characterization of heterojunction between polyaniline titanium dioxide tetradecyltrimethylammonium bromide and n-silicon

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ABSTRACT

The organic/inorganic semiconductor heterojunction has been fabricated by thin film formed on n-Si semiconductor substrate using spin coating technique from the solution of polyaniline (PANI) titanium dioxide (TiO_2) composite chemically synthesized in the presence of the cationic surfactant, tetradecyltrimethylammonium bromide (TTAB). The thickness of the polymeric film coated on the n-Si substrate has been found to be 110 nm by using the profilometer. The current–voltage (*I–V*) characteristics of the PANI TiO_2 TTAB/n-Si heterojunction have been measured in the temperature of 178–238 K. The *I–V* characteristics of the PANI TiO_2 TTAB/n-Si heterojunction have shown the rectifying behavior. The forward *I–V* characteristics of the device have been analyzed on the basis of the standard thermionic emission (TE) theory. An abnormal increase in the barrier height and decrease in the ideality factor with increasing temperatures has been shown. This behavior has been interpreted assuming inhomogeneity of barrier formed at the interface. The temperature-dependent *I–V* characteristics of the PANI TiO_2 TTAB/n-Si heterojunction have revealed a double Gaussian distribution giving mean barrier heights of 0.916 eV and 1.164 eV and standard deviations of 0.114 eV and 0.131 eV, respectively. Furthermore, the PANI TiO_2 TTAB has been characterized by using Fourier Transform Infrared (FTIR), Ultraviolet–visible (UV–vis) spectra and X-ray diffraction analysis (XRD).

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1. Introduction

In recent years, conducting polymers have become known as a new kind of materials for the advanced technology and solid state devices. The electrical conductivity of these polymers can be change from insulating to metallic by chemical or electrochemical doping [1–4]. The conducting polymers can be used as the active layer in organic light emitting diodes (OLEDs) [5,6], organic field effect transistors (OFETs) [7], solar cells [8], photodiodes [9], gas sensors [10,11], optical sensor [12] and memory devices [13]. These devices are being pushed toward commercialization because they can be fabricated by inexpensive techniques, such as spin coating, ink-jet printing, low temperature fiber drawing and screen-printing on the substrates. This leads to a real advantage over the expensive and sophisticated technology used with inorganic materials in the semiconductor manufacturing [1].

A large number of Schottky barrier diodes (SBDs) have been prepared using conducting polymers with metals and inorganic semiconductor [14–18]. The electronic properties of a metal/semiconductor (MS) or Schottky barrier diodes (SBDs) are characterized by its barrier height. The barrier height (BH) is the difference between the edge of the respective majority carrier band of the semiconductor and the Fermi level at the interface. SBDs show an exponential and asymmetrical behavior of the *I–V* curves.

Among various conducting polymers, polyaniline (PANI) has been extensively studied because it has a broad range of tunable properties derived from its structural flexibility for electronic and optoelectronic applications [1]. The various combinations of polyaniline could be synthesized, and they have different properties. On the basis of PANI, the fabrications of optoelectronic and microelectronic devices such as diodes and transistors have been reported [19–23]. Stable field effect transistors have been fabricated using water-soluble self-acid doped conducting polyaniline and sulfonic-acid ring substituted polyaniline [23]. The change in

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the electrical conductivity of conducting polymers as a function of exposed gases has been stimulated interest in these materials as active components in electronic devices as well as gas sensors [11]. The junction parameters such as the ideality factor and barrier height have been influenced by the methane gas. The interaction of the polypyrrole (PPy) has been explained by change in the barrier height and in the carrier concentration of the diode [11]. Most of conducting polymers are sensitive to the environment, and their electrical properties tend to deteriorate over time due to over oxidation, moisture, high temperature and chemical alteration. Moreover, the low mechanical strengths of the conducting polymer restrict their potential application in device fabrication [24].

Composite of conducting polymer with insulating polymers are likely to yield conductive polymeric materials with improved mechanical strengths, while retaining their high electrical conductivities and other properties. Schottky barrier diodes of PANI and composite of PANI with polystyrene have been fabricated using indium as Schottky contact and platinum as ohmic contact. It has been observed that the composite materials have better mechanical strength as well as the diode quality than that of the pure polymer [25].

Recently, PANI has been attracted considerable attention for the preparation of its composites with inorganic particles to improve their processability [26–28], such as sulfonated polyaniline (SPANI)/TiO_2 [29], PANI/SnO_2 [30], PANI/para-toluene sulfonic acid (pTSA)-TiO_2 [31]. p-PANI/n-TiO_2 heterojunction has been fabricated for liquefied petroleum gas (LPG) sensor in a room temperature [32]. The gas sensing properties of heterojunction to LPG have been indicated that the p-PANI/n-TiO_2 heterojunction was a candidate for LPG detection. Additionally, PANI/TiO_2 based structures have received much attention owing to their high current production in an external circuit by excitons dissociation at the TiO_2 and conjugated polymer interface. These heterojunction structures confirmed high charge separation and charge carrier transport through the metal oxide and the hole conducting materials respectively. For efficient conducting polymer/metal oxide based heterojunction structure, an important challenge is preventing the recombination of excitons. The charge separation and charge transfer at the interface heterojunction is an essential factor for determining the performance of heterojunction structure. These factors are mainly related to the morphology, uniformity, and interconnection of both the layers of the heterojunction thin film. Surfactants can improve properties of the heterojunction thin films.

In this work, PANI TiO_2 TTAB/n-Si heterojunction has been prepared by deposition of PANI TiO_2 TTAB thin films using the spin coating technique on the chemically cleaned n-Si semiconductor substrate. The temperature dependence of the *I–V* characteristics of the PANI TiO_2 TTAB/n-Si heterojunction has been used to obtain information about the transport mechanisms of the fabricated devices. The characteristics parameters of the heterojunction such as ideality factor and barrier height have been compared with the other polymeric devices.

2. Experimental procedures

In the fabrication of the heterojunction, n-type Si wafer with (1 0 0) orientation, one sided polished, 600–650 μm thickness and 0.5–3 Ω cm resistivity has been used. The wafer has been chemically cleaned using the RCA cleaning procedure (i.e., a 10 min boil in $NH_4 + H_2O_2 + 6H_2O$ followed by a 10 min boil in $HCl + H_2O_2 + 6H_2O$) [33]. Before ohmic contact formed on the substrate, the wafer has been dipped in dilute HF:H_2O (1:10) for about 30 s to remove any native-thin-oxide layer on the surface, then rinsed with de-ionized water (purity up to 18.2 MΩ cm) and dried with high-purity N_2 gas. Next, the wafer has been inserted into the deposition chamber immediately after cleaning. The ohmic contact has been made by thermal evaporation Au–Sb (88%, 12%) alloy on the back of the n-Si substrate in a vacuum-coating unit at about 10^{-6} Torr and then it has been annealed at 420 °C for 3 min in flowing N_2 in a quartz tube furnace. Evaporated film thickness has been monitored using a quartz oscillator and the metal films had a thickness of 500 Å.

The chemical synthesize of TiO_2/PANI composite in an aqueous medium containing cationic tetradecyltrimethylammonium bromide (TTAB) has been described in detail in Ref. [26]. Chemical characterization of the PANI TiO_2 TTAB, PANI/TTAB and undoped PANI have been performed by the Fourier Transform Infrared (FTIR), Ultraviolet–visible (UV–vis) spectra and X-ray diffraction analysis (XRD). The FTIR spectra of the samples have been taken by using a Perkin Elmer Spectrum BX FTIR system recorded between 400 and 4000 cm^{-1} with a 4 cm^{-1} resolution from KBr pellets. The UV–vis spectra of the samples have been recorded between 270 and 900 nm using a 1 cm path length quartz cuvette and pure N-methly pyrrolidine (NMP) on a Perkin Elmer Lambda 20 UV–vis spectrophotometer. The X-ray powder diffraction (XRD) data of the samples have been recorded on a computer-interfaced Bruker AXS D8 advanced diffractometer operating in Bragg-Brentano geometry (Cu K radiaotion, graphite monochromator, 40 kV and 40 mA) over a $10^\circ \leq 2\theta \leq 90^\circ$ angular range. The chemically synthesized PANI TiO_2 TTAB has been dissolved in NMP, filtered and then used to form thin films by the spin coating (50 s at 3500 rpm on a Delta6 RC spin coater) on n-Si substrate. The film obtained in this way has been treated with 1 M HCl solution to form the polyemeraldine salt. The thickness of the polymeric films has been measured to be 110 nm by a profilometer. Finally, a circular top metal contact with 550 Å thicknesses has been obtained by high purity (99,999%) gold (Au) thermal evaporation under about 10^{-6} Torr pressure by using shadow mask. Thus, Au/PANI TiO_2 TTAB/n-Si/Au–Sb heterojunctions have been fabricated. The *I–V* characteristics of the device have been performed in the temperature range of 178–238 K, by using an HP 4140B Picoammeter/Voltage Source and a homemade liquid nitrogen cryostat.

3. Experimental results and discussion

3.1. UV–vis, FTIR spectra and XRD results

The UV–vis spectra of the PANI/TiO_2–TTAB, PANI/TTAB and undoped PANI dissolved into NMP have indicated two characteristic peaks as shown in Fig. 1(a–c). NMP, exerting weak base properties, is a good solvent for PANI, where the polymer chains are unfolded. The interaction of NMP and surfactant is so strong that the resulting product is susceptible to dedoping (REF). Thus, PANI and PANI/TiO_2 in the presence of surfactant, TTAB, might exhibit emeraldine base behavior in the UV–vis spectra. In case of doped PANI/TTAB, a blue shift occurs from 575 nm to 630 nm due to the doping process. In spectrum of PANI/TiO_2–TTAB, the first peak 350 nm (λ_1) is attributed to the $\pi \rightarrow \pi^*$ transition in benzenoid ring, the second peak at 550 nm (λ_2) corresponds to the $n \rightarrow \pi^*$ the excitonic transition due to partial oxidation of polymer and can be assigned to represent the intermediate state between leucoemeraldine form containing benzenoid ring and emeraldine form containing the conjugated quinoid ring. It is well known that, in composite systems with PANI, strong guest-host interactions, such as hydrogen bonding, occur in the form of NH···O–Ti in TiO_2 [34,35]. Compared UV–vis spectra of PANI/TTAB and PANI/TiO_2–TTAB in Fig. 1, the peaks of benzenoid and quinoid ring transitions have shifted from 348 and 625 nm to 350 and 550 nm due to intramolecular interaction between PANI and TiO_2 when TiO_2 is added in the

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