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Optical, electrical and photovoltaic characteristics of organic semiconductor based on oxazine/n-Si heterojunction

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ABSTRACT

In this work, the construction and photoelectrical characterization of p-type organic semiconductor oxazine (OXZ) in junction with n-type silicon semiconductor are presented. The Stokes shift between absorption and emission of oxazine was analyzed. The analysis of the spectral behavior of the absorption coefficient (α) of OXZ, in the absorption region revealed a direct transition, and the energy gap was estimated as 1.82 eV. From the current–voltage, *I–V*, measurements of the Au/OXZ/n-Si/Al heterojunction in the temperature range 300–375 K, characteristic junction parameters and dominant conduction mechanisms were obtained. This heterojunction showed a photovoltaic behavior with a maximum open circuit voltage, $V_{oc,}$ of 0.42 V, short-circuit current density, $J_{sc,}$ of 3.25 mA/cm^2, fill factor, *FF*, of 0.35 and power conversion efficiency, η, of 3.2% under 15 mW/cm^2 white light illumination.

1. Introduction

During the last decade, focus on organic photovoltaics (OPV) devices has increased due to their low cost, low thermal budget, solution processing, flexible substrates, operational stability, very high speed of processing, environmental impact and indoor applications [1–4]. Until recently the silicon-based PVs had advantages in both efficiency and lifetime of the device for monocystalline silicon devices. Organic solar cells have the potential to be competitive on the photovoltaic power market due to expected low production costs even with lower efficiencies and shorter lifetimes compared to their inorganic counterparts [4,5]. It should be emphasized that high efficiency and long lifetime has not been observed for the same device, and one of the current challenges is the combination of all the desirable properties in the same material (efficiency, stability, processability and low cost). The separate demonstration of these properties for different materials, however, does show that it should be possible and from this point of view, the OPVs could become a true competitor to the silicon-based PV.

Heterojunction-based semiconductor devices formed by organic compounds grown on inorganic substrates have extensively been investigated by many researchers for their potential use in the electronic and optoelectronic technologies so far. Namely, many devices using the polymeric [6–9] and nonpolymeric organic materials [10–12] have been fabricated including light-emitting diodes and Schottky-type devices like an inorganic semiconductor/organic semiconductor material or a metal/organic semiconductor material, and their electrical and photoelectrical properties have been investigated for more than three decades. Organic materials have a wide application in thin-film electronics; one of their main advantages is the fact that they can be produced in large quantities by simple techniques such as spin coating, which lowers the production cost dramatically [13]. In recent years, power conversion efficiencies of thin-film organic photovoltaic cells have been increased steadily and rapidly [14,15]. Although higher power conversion efficiency is provided by conventional silicon-based photovoltaic devices, a large number of scientists are involved in the development of organic molecules and conjugated polymer-based photovoltaic devices [16–18].

Oxazine (OXZ) dyes have been a subject of much spectroscopic research due to their great use as a tunable laser dye in the range 600–900 nm. Alternatively, they are also the standards for fluorescence studies and are of significant value as biological probes [19]. A large number of investigations have been carried out in recent years on spectroscopic behavior of this group of dyes [20,21].

In this paper, we report the fabrication and electrical properties of rectifying heterojunction barriers using oxazine as an interlayer formed on n-Si substrate. Our aim is to study the optical

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and fluorescence properties of oxazine films. We also study the suitability and possibility of organic-on-inorganic semiconductor contact barrier diodes for use in barrier modification of Si metal–semiconductor diodes using *I–V* and *C–V* characteristics of oxazine/n-Si heterojunction. The characteristic parameters of these devices have been obtained from their dark current–voltage and capacitance–voltage characteristics. Photovoltaic characteristics of oxazine/n-Si heterojunction under different intensities of white light illumination were also studied.

2. Experimental details

2.1. Materials

The oxazine compound, whose molecular structure is shown in Fig. 1, was purchased from AnaSpec Inc., and used without further purification as a solute. The oxazine dye appears as green bronzy crystals. The junctions have been prepared using a polished n-type Si wafer with (1 0 0) orientation and electron concentration $10^{16}\,cm^{-3}$ with thickness 400 μm obtained from Nippon Mining company (Japan) as a substrate.

2.2. Solubility and stability

The oxazine dyes showed good solubility in water, ethanol and DMSO. They were found to be more photo and thermal stable than similar commercially available materials.

2.3. Processes and fabrication of the device

In order to remove the native oxide on surface of n-Si, the substrate was etched by a solution of $6HNO_3$:1HF:$35H_2O$ for 20 s, then rinsed with deionized water and dried. The n-Si substrates were coated from one side by oxazine thin film using spin coating process. The coating solution was dropped onto substrate, which was rotated at 2000 rpm for 30 s. After the spin coating, the film was dried at 350 K for 10 min in a furnace to evaporate the solvent and to remove organic residuals. The front contact of this heterojunction was made with gold mesh electrode. The active area of the fabricated heterojunction was about $0.20\,cm^2$. The back contact was made by depositing a relatively thick film of Al to the bottom of the n-Si substrate using thermal evaporation technique under vacuum (Edwards, E306A) at pressure about 10^{-4} Pa. Thus, an Au/OXZ/n-Si/Al junctions were obtained. The fabricated cells were annealed in air at 373 K for 1 h to complete the junction formation. The schematic diagram of the fabricated junction is shown in Fig. 2.

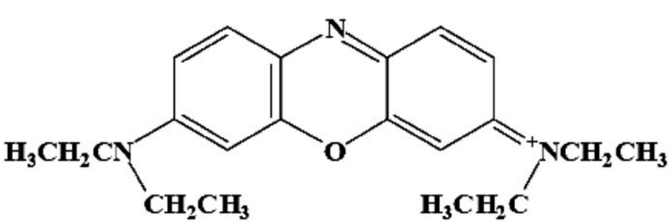

Fig. 1. Molecular structure of the OXZ organic semiconductor.

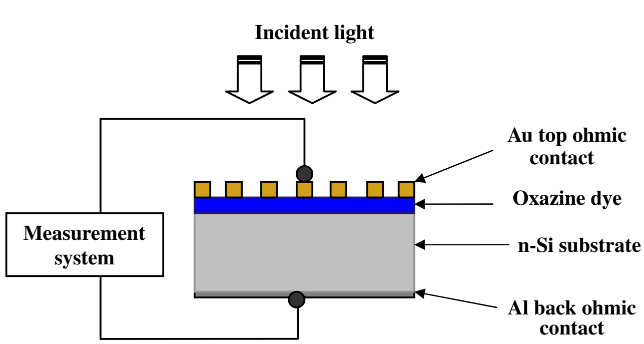

Fig. 2. Schemtaic diagram of Au/OXZ/n-Si/Al heterojunction.

2.4. Methods and characterization tools

The absorption studies in the UV–vis spectra of the OXZ films deposited on a quartz substrate were recorded on a JASCO-570 UV/VIS/NIR spectrophotometer. Fluorescence was read on a spectrophotometer (Perkin Elmer L550B; Perkin Elmer, Wellesley, MA, USA) using excitation/emission settings of 700/900 nm.

The electrical measurements were performed using a conventional d.c. technique and a high-impedance Keithley 617 electrometer. The room temperature *C–V* measurements of the device were achieved at 1 MHz by using computerized *C–V* meter (model 4108, solid-state measurements, Inc. Pittsburg Pennsylvania) in air and at dark conditions. The temperature was measured directly by means of chromel–alumel thermocouple connected to a hand-held digital thermometer. The incident power density of light illumination was $15\,mW/cm^2$ provided by a halogen tungsten lamp. Optical exposure was focused onto the Au electrodes from above the devices. The power density of illumination on the device was measured by means of a calibrated TM 20 solar power meter.

3. Results and discussion

3.1. Optical absorption characterization

The UV–vis spectrum spectra of OXZ films at room temperature (300 K) is shown in Fig. 3. It is observed that there is an absorption peak namely the Q-band in the wavelengths range 590–645 nm and a small peak at shorter wavelengths in the UV region termed Soret band (B-band) in the range 239–295 nm. The absorption peaks can be readily interpreted using the Gouterman's four-orbital model [18]. Specifically, there are two principle π–π* transitions of the oxazine ring: a lower energy

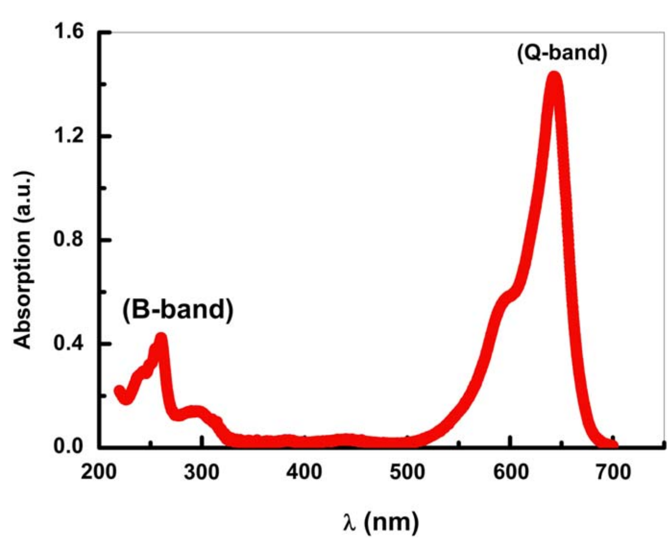

Fig. 3. The UV-vis absorption spectra of OXZ films at 300 K.