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Electrical transport mechanisms and photovoltaic characteristics of Au/neutral red/p-Si/Al heterojunction solar cell

H.M. Zeyada [a], M.M. Makhlouf [b,c,*], M.M. El-Shabaan [a], M.H. Zeyada [d]

[a] Department of Physics, Faculty of Science, University of Damietta, 34517 New Damietta, Egypt
[b] Department of Physics, Faculty of Applied Medical Sciences at Turabah, University of Taif, 21995, Saudi Arabia
[c] Department of Physics, Damietta Cancer Institute, Damietta, Egypt
[d] Department of Computer Engineering and Systems, Faculty of Engineering, University of Mansoura, 35516, Egypt

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ABSTRACT

Uniform thin films of neutral red, NR, have been successfully prepared by thermal evaporation technique. X-ray diffraction patterns showed that the structure of NR film consists of nanocrystallites dispersed in amorphous matrix. Increasing annealing temperature influences crystallite size and quantity of amorphous phase. The high absorption of NR films in visible region of spectra supports the application of NR film as an absorber in photovoltaic devices. Hybrid organic–inorganic heterojunction solar cell, Au/NR/p-Si/Al, was fabricated. The current–voltage characteristics of the heterojunction diode have been studied in the temperature range of 300–355 K and in the voltage range (−2 to 2 V). The device showed a series resistance of 2.64 kΩ, shunt resistance of 237 kΩ, rectification ratio of 106 at ±1 V and ideality factor of 1.8 at room temperature. It was found that the conduction mechanisms of the diode are controlled by the thermionic emission at forward voltage bias ≤0.2 V and space charge limited current (SCLC) conduction in the voltage range $0.2 < V \leq 2$ V. The capacitance–voltage characteristics of the NR/p-Si device were studied at room temperature in dark condition. Energy band diagram for NR/p-Si device was constructed. The device under illumination with light of intensity 20 mW/cm^2 gives values of photovoltaic parameters as: open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (*FF*) and power conversion efficiency (η) are 0.46 V, 1.78 mA, 0.29 and 2.37%, respectively.

1. Introduction

In recent years, the photovoltaic technology has a growing research interest due to the increasing demand for renewable and clean energy. Dyes are promising organic materials for applications in liquid crystal displays [1], photovoltaic cells [2], sensors [3] and it is used in dye sensitized solar cells (DSSCs) [4,5]. The DSSC is distinguished in that it resembles natural photosynthesis in two respects: it uses an organic dye to absorb light and produces a flow of electrons and multiple layers to enhance both the absorption and efficiency of the DSSC. Investigations of organic–inorganic heterojunction devices attract some interest due to both the unusual nature of these contacts as well as to the potential new devices that can be applied. Recently, different organic–inorganic heterojunctions such as pyronine-B /Si [6], b-carotene/Si [7], chitin/n-Si [8], and MEH-PPV/p-Si [9] have been fabricated and then the electronic parameters have been measured in each fabricated junction.

Organic thin films have several clear advantages over inorganic thin films such as large-area coverage, mechanical flexibility, low-temperature process capability, easy preparation and low cost. Neutral red, NR, is an organic dye belonging to the phenazine family that are mainly used as aromatic dyes [10]. NR was first prepared by Witt [11] via condensation of p-nitrosodimethylanaline and 2,4-daimino-toluene in aqueous medium and oxidization of the resulting toluylene blue by ferric chloride. NR, dye which is used in the present work has molecular formula $C_{24}H_{28}N_3Cl$. The structure skeleton of NR has an extended π-conjugation system due to the delocalization of electrons in the benzene, methyl and amine functional groups and that leading to a wide range of high optical absorption in visible spectrum. NR is thermochromic [1,12] and photochromic [1,13] materials. Influence of γ-ray irradiation on the spectral characteristics and absorption spectrum of NR thin films deposited by thermal evaporation technique have been studied [14]. The type of electron transition and energy band gap, optical constants, optical dispersion parameters and dielectric constants of NR thin films were also measured. All of these studies showed that NR compound has a high optical absorption in visible region of spectrum with onset band-gap of 1.75 eV that recommend them to be used in optoelectronic device fabrication [14]. The application of NR in solar cell fabrication process will be provided as thin film sandwich. The sandwich may be constructed in homo- or heterojunction configuration. Such homojunction devices have loss factors including; photo carrier generation is a function not only of bulk optical

* Corresponding author at: Department of Physics, Faculty of Applied Medical Sciences at Turabah, University of Taif, 21995, Saudi Arabia.
E-mail addresses: m_makhlof@hotmail.com, m.m.makhlouf@hotmail.com (M.M. Makhlouf).

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absorption, but also of available mechanisms for exciton dissociation, non-irradiative recombination at the interfaces and non-geminate recombination at impurities. Single layer solar cells of this type deliver quantum efficiencies of less than 1% and power conversion efficiencies of less than 0.1% [15]. In heterojunction devices, the local electric fields are strong and may break up photo generated exciton provided that the differences in potential energy are larger than the exciton binding energy. The organic donor–acceptor interface separates exciton much more efficiently than the organic/metal interface; efficient photovoltaic devices may be made from heterojunction configuration.

To our knowledge, NR is one of the less reported dyes in literatures. The electrical properties of NR thin films have not been investigated yet. In the present work, the attention has been focused on fabricating a hybrid heterojunction solar cell of Au/NR/p-Si/Al and providing an investigation about its electronic transport mechanisms and photovoltaic properties.

2. Experimental details

A brownish-black powder of NR (IUPAC name: 3-Amino-7-dimethylamino-2-methylphenazine hydrochloride) was purchased from Sigma-Aldrich Co. (USA) and was used in as-received condition without any further purification.

NR thin films of thickness 407 nm were prepared by thermal evaporation technique. The high vacuum coating unit was used for this purpose. Initially, the pressure inside the vacuum work chamber was pumped down to 10^{-5} mbar. Evaporation of the NR material is carried out with quartz crucible heated by boat-shaped molybdenum heater while Au and Al electrodes were thermally evaporated by using basket-shaped tungsten filament. Rate of deposition and film thickness were controlled by using quartz crystal thickness monitor. The deposition rate was controlled at 2.5 Å/s.

The X-ray diffraction, XRD, patterns for NR as thin film were performed by a diffraction system utilizing CuK_α radiation (λ = 1.5418 Å). The X-ray tube current is 30 mA and the applied potential is 40 kV. Thin films of NR were annealed at different annealing temperatures in a tubular vacuum furnace with a soaking time of 1 h.

The hybrid Au/NR/p-Si/Al solar cell was fabricated by thermal evaporation of NR and Al electrodes on the surfaces of p-Si substrate. NR was deposited on polished surface of Si substrate and Al was thermally evaporated on rough surface of Si substrate. A mesh of Au electrode was thermally deposited on the surface of NR. The Si substrate is a p-type single crystal wafer with one polished face, the hole concentration of p-type Si single crystal wafer is 1.6×10^{23} m^{-3} and its thickness is 400 μm. First, the p-Si wafer was chemically cleaned and etched by PC4 solution (HF: HNO_3: CH_3COOH in ratio 1:3:1) for 10 s, then rinsed with deionized water and isopropyl alcohol and oven-dried. The hybrid junction of Au/NR/p-Si/Al solar cell was fabricated according to the following steps; the back contact electrode was made by depositing a relatively thick film of pure Al to the p-Si substrate. NR with thickness of 95 nm was deposited on the front surface of p-Si wafer. Then, a front of pure Au was evaporated on NR layer as a mesh grid electrode. The active area of the solar cell is 0.5 cm^2.

The electrical resistivity of NR films was measured by high impedance electrometer. The independent stabilized DC power supply of the electrometer was used as a power supply. All measurements were taken in dark at different temperatures in ambient atmosphere. The current–voltage, I–V, characteristics of the virgin heterojunction device were measured under dark and illumination conditions for different annealing temperatures. The incident power density of light illumination provided by tungsten filament lamp was 20 mW/cm^2. The intensity of the incident light was measured by using a digital lux-meter.

The UV–vis absorption spectra of NR thin film deposited onto optically flat fused quartz substrates were recorded by spectrophotometer. All these spectra were recorded at room temperature.

The capacitance of the NR/p-Si cell was measured at a high frequency of 1 MHz using a computerized meter in dark and at room temperature.

3. Results and discussion

3.1. X-ray diffraction patterns for NR

The X-ray diffraction, XRD, pattern for NR in powder form is given elsewhere [14]. Identification of XRD pattern of NR in powder form was performed by using [16,17] and it showed that it has a triclinic crystal system and space group p1 with lattice parameters: a = 10.27 Å, b = 14.77 Å, c = 16.45 Å, α = 72.67°, β = 111.61° and γ = 81.83°. The XRD pattern for pristine thin film of NR of thickness 407 nm is illustrated in Fig. 1; a single diffraction peak at ($2\theta = 25°$) corresponding to diffraction from ($1\ \bar{3}0$) superimposed on amorphous phase is observed.

The effect of annealing temperatures on the XRD patterns of the NR thin films with thickness 407 nm is shown also in Fig. 1. The assignment of diffraction peaks in Fig. 1 was obtained from XRD pattern of polycrystalline powder [14]. Annealing at 343 K did not affect the peak position of diffraction ($1\ \bar{3}0$) of pristine NR film and slightly increased its intensity. Annealing NR films at 443 K nucleates a new diffraction peak at ($2\theta = 31.75°$) corresponding to diffraction from (1 5 0) and a halo at 2θ angular range of 14–38°; this indicates partial transformation of nanocrystallite NR phase into amorphous one. Changes in the intensities of X-ray diffraction peaks may result from grain growth and large amounts of intrinsic stresses, the stresses resulting at the early stages of growth; the magnitude of these stresses depends upon both the film thickness and annealing temperatures.

The mean crystallite size, D, of the film was estimated by using the Scherrer expression [18]. The calculated crystallite size of nanocrystals in pristine film is 97 nm. In annealed NR film (343 K with a soaking time of 1 h); the sharp diffraction peak corresponds to reflection from ($1\ \bar{3}\ 0$) is retained and the amount of amorphous phase of NR is significantly decreased. The calculated crystallite size is 17 nm. Increasing annealing temperature to 443 K increases the amount of amorphous phase and a new diffraction peak appeared corresponding to diffraction from the (1 5 0). The determined crystallite size [18] for the annealed film at 443 K is 100 nm.

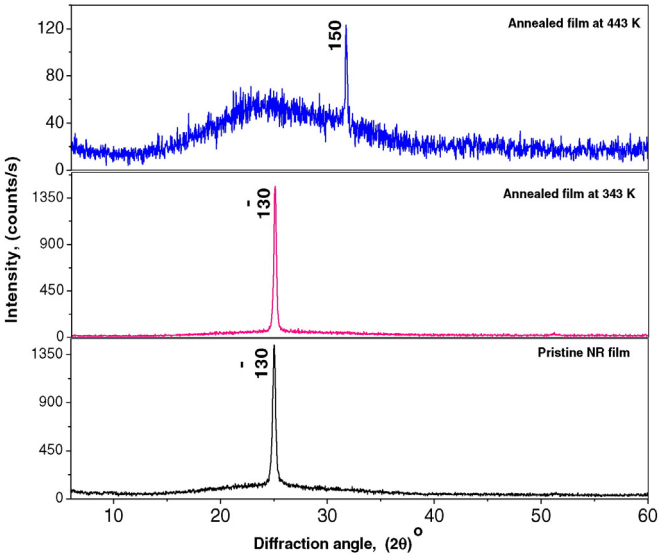

Fig. 1. XRD pattern for pristine and annealed NR films.