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Infiltration of CdTe nano crystals into a ZnO wire vertical matrix by using the isothermal closed space technique

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ABSTRACT

A ZnO nanorod structure was grown by the hydrothermal method and interpenetrated with CdTe using the isothermal closed space sublimation technique. The obtained structure was studied by using the Rutherford backscattering spectrometry (RBS), Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HRTEM). The X-ray Diffraction (XRD) technique confirmed the presence of CdTe nanocrystals (NCs) of very small size formed on the surface and in the interspaces between the ZnO nanorods. The RBS observations together with the SEM observations give information on the obtained structure. Finally the photoluminescence studies show a strong energy confinement effect on the grown CdTe NCs.

1. Introduction

Nowadays, an efficient conversion of the solar energy into electric energy is one of the key issues for the photovoltaic solar cells industry. The development of alternatives to fossil fuels is of utmost importance for the future of the planet. As a consequence, this subject has strongly drawn the attention of the scientific community in the past 10 years.

In photovoltaic solar cells, electron-hole (e-h) pairs are created following photon absorption. These pairs are separated from the lattice due to the different potential barrier in the junction zone made up of semiconductor materials conveniently selected for this particular purpose. However, not all e-h pairs separated in this way will lead to electrical currents that feed some load connected to the photovoltaic device, This is due to the different recombination processes which decrease the number of effective charge carriers and, in turn, the conversion efficiency.

One possible way to decrease recombination losses and therefore to increase the solar cell efficiency is to reduce the transport path of electrons and holes through the absorber material into the extraction zone of the cell. Moreover, an extra improvement in the cell efficiency would be achieved if the effective area of the solar cells where the excitons are created or e-h pairs are photo-excited is increase significantly. Both features seems to be an excellent way to compensate and reduce the loss of charge carriers. This idea has been realized in some heterostructures using the morphology of aligned ZnO nanorods. In some cases, the space between the nanorods was refilled with a suitable polymer or alternatively the surface of the nanorods was covered with an inorganic semiconductor material [1]. Also were used only inorganics semiconductor materials for compound the heterostructure [2,3].

It has been shown that ZnO is a useful semiconductor material for solar cells due to its intrinsic properties [4]. It has an energy gap around of E_g = 3.3 eV, which makes it quite transparent to the solar radiation. Moreover, the structure conformation of ZnO nanorods is easily obtainable through several techniques, in particular with the hydrothermal method [5,6]. The production of a solar cell based on aligned ZnO nanorods requires some material that provides the necessary potential to produce e-h separation and to extract the holes properly. The filling of the ZnO nanorods interspace with polymers is a possibility that has been already explored but it leads to a different energy conversion mechanism starting by photon absorption and exciton formation. Immediately the exciton

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dissociation must occurs in order that the charge transport will start up [7,1]. Moreover, this type of cell, namely filled with organic materials, has other disadvantages like fast degradation.

Solar cells based solely on inorganic materials have proved to be durable and stable during operation. The CdTe is a good material to refill the ZnO nanorods matrix since it has a gap around of 1.5 eV at room temperature, which makes it an excellent radiation's absorber for solar light that cross the ZnO window. Moreover, CdTe is a natural p-type semiconductor without intentional doping since Cd-vacancy formation takes place during its growth [8]. For this reason, CdTe presents good hole transport properties while a type II band alignment stems from the interaction between ZnO and CdTe. Indeed, type II band alignments for ZnO/CdTe should facilitate electron transfer from CdTe to ZnO to ITO, thus enhancing the capabilities in photovoltaic cells. Finally, it is worth mentioning that the mismatch between CdTe and ZnO is relatively small, which enhances the electron injection in a photovoltaic device thought the presence of heterojunctions with defects, interfacial layers and grain boundaries [9].

In this scenario, it must be pointed out that filling up completely the space between the nanorods is a difficult task and the results obtained so far are limited [10,11,12,5]. The vapor deposition based techniques are a good option for the spatial refilling between the nanorods. However, the more common techniques of these types cannot achieve the desired effects because the growth of the material deposited inside tiny spaces like those between ZnO nanorods may lead to an obstruction of the entrance after a short exposition time, thus hampering the complete filling of the cavities. The isothermal closed space vapor deposition technique proved to be very effective for solving this kind of problem as shown in previous works [13].

In this work, the isothermal closed space vapor deposition technique is used in order to obtain ZnO nanorods filled up with CdTe. It is demonstrated that the crystalline structures of CdTe are small enough to present a strong energy confinement of excitons. This fact makes may have a positive impact on the photonic efficiency and to the overall performance of solar cells.

It should be pointed out that the present work deals with the material growth and characterization of the CdTe/ZnO heterostructure.

2. Experimental section

The ZnO nanorods were obtained by using the hydrothermal technique. Conductive glass substrates (ITO, 10 ohm/square) were ultrasonically cleaned with acetic acid, acetone and isopropanol. The clean substrates were 2 times spin coated with a solution of 5 mM zinc acetate dehydrate in ethanol at 2000 rpm during 20 s.

The spin coated substrates were located in a close oven at 350 °C during 20 min, process that give place to the formation of small grains of ZnO on the substrate's surface. Then, the activated substrates were immersed in a solution prepared by using a 1:1 ratio of zinc nitrate and hexamethilenetetramine (HMT) as precursors. Finally the ZnO nanorods were grown over glass or ITO substrates at a temperature of 90 °C for 90 min. In sequence they were introduced in an isothermal closed spaced sublimation system. Details of this apparatus are displayed in Fig. 1 and described in Refs. [14,15]. The substrate with the ZnO nanorods was located in a way to bring them horizontally over the sources and the purge hole. A furnace around the quartz tube keeps the whole system at an almost constant temperature between 350 °C and 400 °C.

The substrates were exposed alternatively to Cd and Te vapors coming from high purity (99.9%) solid sources. The exposure to these sources was of 60 s each step. Between exposure from one source to the next one, the structure was exposed to an atmosphere of high purity inert gas during a time that range between 3 and 60 s, (purge process). The process of exposure to the sources and purge is repeated cyclically N times ($30 < N < 160$). Table 1 contains details about the purge time and cycle numbers used during the growth of CdTe over ZnO nanorods by ICSS.

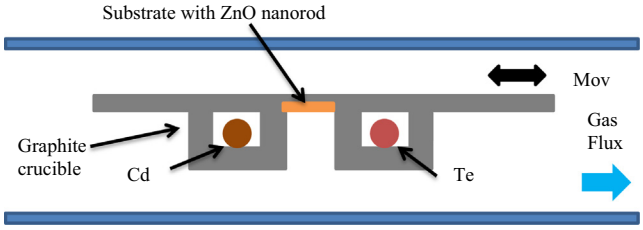

Fig. 1. Graphite crucible placed into quartz reactor. This has cavities for the sources of vapor and a hole for vapor purge. The substrate with the ZnO nanorods is placed alternatively over the vapor sources and over the purge hole. The times used and the cycles for each sample are summarized in Table 1. The furnace around the quartz tube maintained the temperature for whole system almost constant.

X-ray diffractograms, Rutherford backscattering (RBS) spectra, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) images, and photoluminescence spectra were measured in all the samples. X-ray diffraction (XRD) patterns were taken in Bragg Brentano configuration using a Siemens D-5000 powder diffractometer with Cu K1 radiation. The deconvolution for microstructural analysis was done with a B_6La certified sample.

RBS measurements were performed at the 3 MV Tandetron accelerator facility of the Ion Implantation Laboratory (Institute of Physics, Federal University of Rio Grande do Sul). For these measurements a 6.6 MeV α-particles were delivered by the accelerator and typical currents were of the order of 20 nA. Backscattered particles were detected by a Si surface barrier detector placed at 170° with respect to the beam direction. The energy resolution of the detector and associated electronics was of 12 keV. In order to determine the compositional profiles the RBS spectra were simulated using the SIMNRA program [16].

SEM images were obtained with a Hitachi S4800 electron microscope. HRTEM observations were performed using a JEOL JEM-2010 (High resolution mode: 0,16 nm point to point).

Photoluminescence spectra obtained at room and low temperatures were acquired using a Crylas CW 266 nm laser as excitation source. The laser power was kept at 8 mW and the signal was collected by a CCD camera PIXIS 256BRUV attached to a grating monochromator. The temperatures of the samples were varied between 16 and 300 K using a Janis Cryostat.

3. Results and discussion

Fig. 2 is an outline of the heterostructure studied in the present work in which the ZnO nanorods are interpenetrated with CdTe. For achieving this purpose a 1 to 3 μm thick layer of ZnO nanorods were grown over bare glass or ITO substrates. Fig. 3(a) and (b) show SEM images of planar view and cross section of pristine ZnO nanorod layers respectively. The estimation of the nanorod dimension and glass coverage was performed using the digital

Table 1
Purge times and quantity of cycles for each sample.

Sample	t purges (s)	Cycles	Substrate
A	3	15	Glass
B	3	30	Glass
C	3	120	ITO
D	3	160	ITO