HRTEM AND X-RAY DIFFRACTION STUDY OF CdTe NANOCRYSTALS DEPOSITED ONTO A ZnO NANORODS LAYER

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A ZnO nanorods 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 Scanning Electron Microscopy (SEM) and High Resolution Transmission Electron Microscopy (HRTEM), which confirm the formation of CdTe nanocrystals (NCs). X-ray diffraction shows clearly the interpenetration of CdTe on ZnO nanotubes and their purity. Structural details, in particular concerning the interface between CdTe nanocrystals and the ZnO nanorods, are revealed by the HRTEM images. The obtained structure in this work could have the potential to increase the photon conversion energy by multiexcitonic generation.

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1. Introduction

Nowadays, the research is oriented towards improving the properties of materials and on the development of new ones. Of particular interest is the use of nanomaterials since it is possible to modulate their properties (physicochemical or mechanical) by interacting on their sizes. Design processes to control the morphology, size and size distribution of the nanoparticles during their elaboration is thus necessary. These processes must also take into account the environmental aspect, must be inexpensive, while allowing large-scale production of a wide range of nanomaterials to meet the demand of different sectors of activity, especially that of photovoltaic cells.

For this purpose, it is important to develop new low cost concepts in order to increase energy conversion efficiencies and economically compete with silicon. This can be achieved by using complex structures (like nanowires) or materials more suitable than silicon for photovoltaic applications.

In order to reduce production costs while maintaining the yield, other materials have been considered for the manufacture of photovoltaic cells. By using direct gap semiconductors such as CdTe, which absorbs light more efficiently than silicon, it is possible to limit the thickness of solar cells and thus to use less of matter. Thus, for charges moving over a smaller distance, the diffusion length of the charge carriers is reduced, which makes it possible to increase the conversion efficiency. The costs of manufacturing and purification are therefore reduced.

Among the most prominent inorganic absorbers of sunlight, cadmium telluride (CdTe) appears to be a good and very interesting candidate. Indeed, CdTe has a high optical absorption coefficient (10^4 cm^{-1}) and narrow band gap of 1.6 eV [2, 3] corresponding to the preferred range of the solar radiation spectrum. In addition, it can form a band II band alignment with ZnO [5].

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Indeed, ZnO is a direct gap II-VI semiconductor whose band gap value is 3.4 eV to 300K [5, 6], which corresponds to an absorption threshold of approximately 380 nm.

2. Experimental methods

The method for sample synthesis

ZnO nanorods samples were obtained according to the method described in [1]: layers of ZnO nanorods were obtained by the hydrothermal method, and deposited in a 2 steps process on a conductive glass substrates (“ITO glass”, 10 ohm/square) first ultrasonically cleaned with acetic acid, acetone and isopropanol. The first step consists of creating “ZnO seeds” on the glass surface, by using a solution of zinc acetate dehydrate in ethanol, spin coated at 2000 rpm during 20 s, and followed by a thermal treatment at 350 °C during 20 min. During the second step, the thus obtained layers were immersed in a solution of zinc nitrate and hexamethilenetetramine (HMT) at 90 °C for 90 min in order to obtain a well organized nanorods layer. Details of preparation are given in [1].

Thereafter the ZnO nanorods were exposed alternatively to Cd and Te vapors coming from solid sources of high purity (99.9%), following the method of isothermal close space sublimation technique (ICSS). Details of deposition of CdTe by this technique are given in [2].

For transmission microscopy and associated HREM studies, the samples have been scratched away from the surface layer using a scalpel and deposited on a copper grid covered with a film of amorphous carbon pierced presenting holes at the edges. Due to the intensity of surface tension forces, many samples remain stably attached. This simple operation allows to find thin grains, enough transparent to incident electrons.

For this purpose, the microscope used was JEOL JEM-2010, with an experimental resolution of 0.23 nm and equipped with an LaB_6 tip.

The X-ray diffraction was performed on the INEL powder diffractometer equipped with a curved linear detector that covers a large angular range of 120°. An Si monochromator ensures the focusing of the beam on the detector. The radiation used is from a Cu anode (K□, λ = 0.154 nm) with a high precision and a real time acquisition. The samples are arranged in vertically positioned capillaries.

3. Experimental results and discussion

Fig. 1 shows the nanorods having a typical hexagonal morphology and satisfying vertical alignment. The dimension of the hexagonal edge to edge is around 200 nm. There are between 40 and 50 nanorods per square micron and the empty space between nanorods occupies around 40 - 45% of the whole surface (Fig. 1).

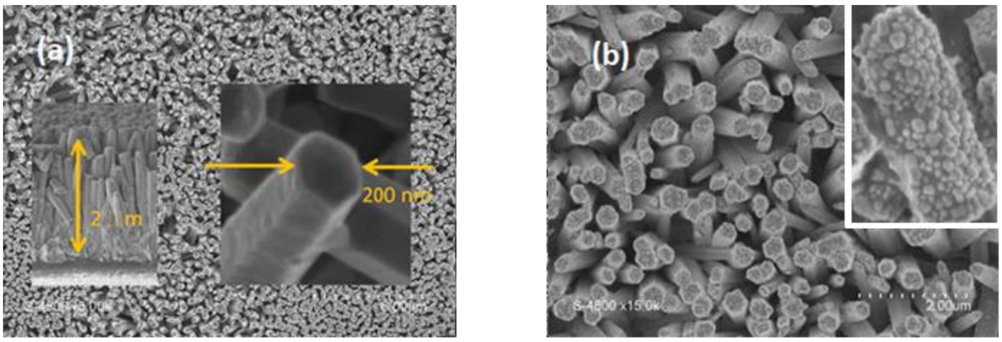

Fig 1. ZnO nanorod (a) before and (b) after infiltration by CdTe nanocristals.

In diffraction mode, the images of the high resolution electron microscopy show a polycrystalline character of CdTe nanoparticles (Fig 2) and a single crystal diffraction pattern of ZnO nanorods (Fig 3).

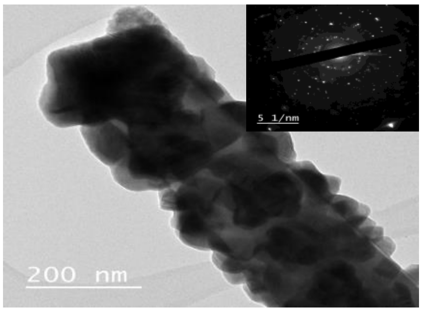

Fig. 2. TEM image of a single ZnO nanorod covered with CdTe nanocrystals and the corresponding diffraction pattern and showing a polycrystalline view of the nanocrystals.

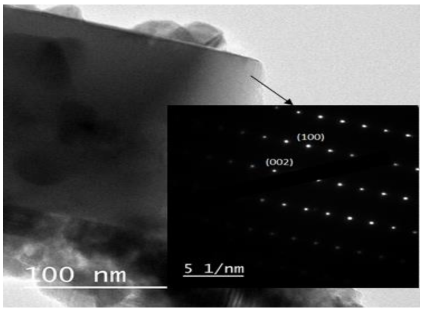

Fig. 3. High resolution electron microscopy image of a ZnO rod and its corresponding diffraction Along the [010] zone axis showing a high crystalline quality.

The image taken from the same ZnO rods (Fig. 3.) contains one set of diffraction spots that can be indexed to the [010] zone axis of the ZnO, and other diffraction spots that can be easily indexed, within the same zone axis, as the (100) and (002) planes (Fig. 3.). For the CdTe [011] zone axis, the associated reflecting planes are $(31\bar{1})$ and (200). The clear diffraction spots within these diffractions show a good crystallinity both of the CdTe nanocrystals in the continuous, polycrystalline covered rod (Fig. 2.) and an isolated CdTe nanocrystals (Figs. 4 and 5). The HRTEM image of the nanocable's tip (Fig. 5c) shows that the top surface of the ZnO nanorod has been also infiltred by CdTe. One may notice that in all of the ZnO/CdTe nanocable samples, the bare ZnO nanorods have the same morphology.

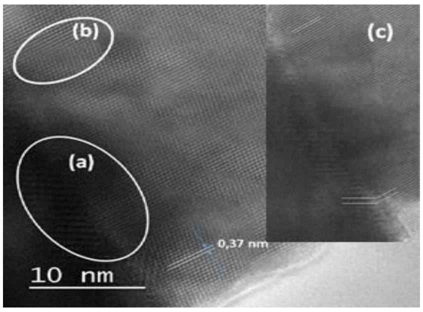

Fig. 4. High resolution transmission electron microscopy image obtained on sample of the CdTe nanocrystal on ZnO. (a) atomic arrangement at the CdTe / ZnO interface showing perfect rearrangement of the periodicy and (b) an isolated microtwin of CdTe nanocristal. (c) represents the magnification at the interface (a) showing the doubling of the CdTe cell parameter at the junction.

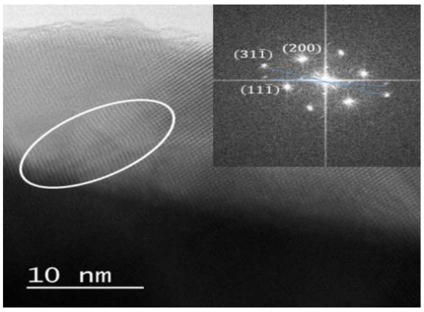

Fig. 5. HRTEM of Frequent observations of twinned domains on the CdTe nanocrystals and its Fourier transform, along [011] zone axis, showing a splitting of the Bragg spot's. The weaker intensity spot is associated to the twinned part of the CdTe nanocrystal.

In Fig. 4, one can see that the coverage of the ZnO rods by the CdTe nanocrystals is realized without any interfacial void formation. The high magnification of other CdTe nanocrystals pattern confirms the previous work done by some of us [1]. Indeed, the image corresponding to the High resolution transmission electron microscopy (Fig. 4 and 5) shows a quite significant contrast variation in the image. We attribute them to the presence of microtwins. The examination of the contrast's image corresponding to Fig. 4a reveals an atomic arrangement of the CdTe / ZnO interface which is done by the intersection of the twinned CdTe with a perfectly monocrystalline atomic arrangement of ZnO. The effect of this reconstruction is reflected in a multiplicity (splitting) of periodicity along the junction line (Fig. 4c). This new periodicity is stabilized by local relaxations, which explains the good adhesion of CdTe on ZnO.

Various models have been examined, the experimental methods likely to confront experience and theory appeared relatively recently. In this field the essential thing had to be provided by electron microscopy since the works of Schober and Baluffi on gold [7] up to high resolution studies [8] more recent but in full development. The X [9] or electron [10] diffraction methods also provide valuable information on the local relaxations and the symmetries of these relaxations.

A study of crystallographic elements, at higher resolution, for CdTe/ZnO is necessary to better understand the mechanisms of relaxation at the interfaces which is still so far from being well understood in these systems.

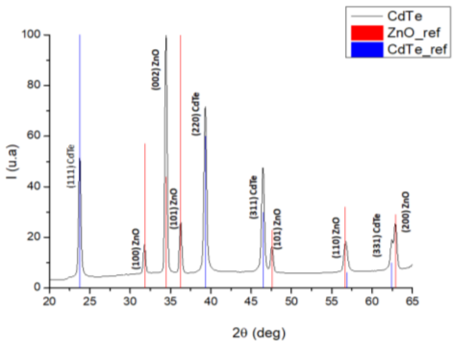

Fig. 6. XRD pattern of ZnO nanorod as infiltred by CdTe nanocrystals.

In addition to the experimental evidence of electron microscopies, concerning the crystalline quality of CdTe / ZnO, X-ray diffraction confirms these observations. Indeed, Fig. 6 on the CdTe / ZnO set, shows a phase purity in the presence with a preferential orientation following (002) for ZnO and (220) for CdTe.

4. Conclusion

In the study we focussed mainly our interest in the characterization by SEM, HRTEM and X-ray diffraction, infiltration of CdTe nanoparticles on ZnO rods obtained by hydrothermal method. Our results clearly show good crystalline quality both of ZnO rods and CdTe nanocrystals. The results of HRTEM reveal a twinning of CdTe nanocrystals similar to that encountered in the bulk materials in its single crystal form.

Acknowledgements

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