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Fabrication of $CuInS_2$/CNTs absorber layers by sol–gel method

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ABSTRACT

In this work, $CuInS_2$/multiwalled carbon nanotube (MWCNT) layers are fabricated by the sol–gel spin-coating method. We introduce two forms of MWCNTs into a CIS_2 solution, washed functional multiwalled carbon nanotubes (W-FMWCNTs) and unwashed-functional multiwalled carbon nanotubes (UW-FMWCNTs), in order to investigate the effects of MWCNTs and an acidic environment on the physical properties of the CIS_2 absorber layers. The structure and morphology of the samples are investigated by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), respectively. The XRD study shows that all samples crystallize in a tetragonal structure. The results obtained from the optical, thermo-electric, and electrical measurements indicate that the two groups of CIS_2 layers prepared using W- and UW-FMWCNTs show the opposite behaviors. The Seebeck coefficient (SC) measurements indicate possible formation of a p–n junction.

1. Introduction

Carbon nanotubes (CNTs) with a stable structure and high thermal resistivity can be considered as a base for some reactions. CNTs are of great interest as catalyst supports in the heterogeneous catalytic reactions due to their high thermal resistivity and conductivity. CNTs with an unrivaled network (tube-shaped) and hollow structure would facilitate the transport of reactants and products. They are also highly resistive in acidic and alkaline conditions [1–7]. CNTs have a hydrophobic surface, and therefore, their suspension in polar solvents is difficult [8–10]. In this regard, adding oxygen-containing groups such as COOH and OH to CNTs has been reported to increase the wetting properties of CNTs [11,12] and diffusion and suspension of the metal particles on their surface [13–16]. These oxygen-containing groups can be considered as an anchor for metal oxides.

On the other hand, much attention has been paid to copper chalcopyrite due to its direct band gap and high absorption coefficient for application as an absorber layer of solar cells [17]. Among the absorber layers based on copper, we can mention CISe, CIS, CIGS, and their alloys, with band gaps in the range of 1.05 to 1.7 eV. CIS_2 has attracted much attention due to its direct band gap of about 1.50 eV, a high absorption coefficient, and short carrier diffusion [18,19]. To the best of our knowledge, there is no published paper on the effect of CNTs doped on the CIS_2 layers. By adding CNTs to a CIS_2 solution, the copper and indium atoms can form complex with the functional groups present on CNTs, and therefore, CNTs

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affect the structural and optical properties of the CIS_2 layers.

The aim of this work is to investigate the effects of multiwalled carbon nanotubes (MWCNTs) doped on the CIS_2 layers. In order to do so, MWCNTs were functionalized at first, and then they were added to the CIS_2 solution. Finally, thin layers of CIS_2 were prepared by the sol–gel method.

2. Experimental

In order to prepare the CIS_2 films, copper acetate monohydrate (Merck, >99%), indium(III) acetate (Aldrich, 99.99%), and thiourea (LOBA chemie, >99%) were used. At first, indium acetate (0.8 mmol) was added to a mixture prepared from propylene glycol (1 mmol), ethanol (2 mmol), and ethanolamine (1.2 mmol). Then the solution was placed on a magnetic heater for 5 min at 70 °C. Subsequently, copper acetate monohydrate (1 mmol) was slowly added to the solution, whose color turned to green. Temperature of the solution obtained was increased to 110 °C, and the solution was then stirred for 10 min. Then diethanolamine (0.6 ml) was rapidly added to the solution, whose color turned to blue. The solution obtained was stirred at the same temperature of 110 °C for 20 min, after which time the temperature was reduced to 50 °C. As a sulfur source, thiourea (4 mmol) was added to the solution, and it was then stirred for 30 min. At the final stage, the solution was cooled to the room temperature, and was aged for 48 h to form a gel.

To functionalize MWCNTs and create carboxylic groups, nitric acid and sulfuric acid were used. This made the pH value for the solution containing MWCNTs to reach about 0.25. After MWCNTs were well-suspended in an acidic solution, due to the intense heat of the process, two processes were considered. Part of the solution was washed in an ice bath to increase the pH value to the neutral one. This solution was used to prepare the layers labeled as group A.

To increase the pH of the functionalized MWCNTs (FMWCNTs) solution, it was poured into a vessel containing ice, which was prepared by triply distilled water. In order to reduce the heat, the side-wall of the vessel was also covered by ice molds. Each time, after melting of the ice molds in the vessel and precipitation of CNTs, the resulting water was replaced by fresh ice molds. This process was carried out to prevent CNTs damaging and breaking the bonds, since the reaction was exothermic. The washing process was repeated for one week until CNTs were suspended in the solution without precipitation. The layers labeled as group B were prepared by the remaining part of the solution without washing.

The washed and unwashed FMWCNTs were labeled as W-FMWCNT and UW-FMWCNT, respectively. Both solutions (W- and UW-FMWCNT) were placed in an autoclave at 60 °C for 40 h in order to dry. The powder obtained from each solution was milled in order to achieve FMWCNTs, which may vary in terms of functionalization.

The functionalization process was performed as follows: an acidic solution containing sulfuric acid and nitric acid, at a ratio of 3:1, was added to MWCNTs and placed in ultrasonic at 60 °C for 3 min to produce carboxylic groups. These groups were formed in the defect places present on CNTs. Therefore, when CIS_2 was combined with FMWCNTs, a complex formed between the copper and indium atoms present in the structures of CIS_2 and carboxylic groups. It should be noted that due to the amount of the defects present in CNTs, the amount of the created carboxylic groups would be different, and only a fraction of CNTs (not all of them) are functioned.

Final solutions were prepared by combination of the CIS_2 gel and W-FMWCNTs at pH 7, and the CIS_2 gel and UW-FMWCNTs at pH 0.25 with the mass ratios of 1:0.5, 1:1, and 1:1.5, respectively. The solutions were aged for 48 h, after which time they were used to deposit layers on the glass substrate by the sol–gel spin-coating method. Spin-coating was repeated for 20 times to achieve the desired thickness. Also to study the supporting layer (only the FMWCNT layer), two distinct layers containing only FMWCNTs with the acidic and neutral pH values were deposited on the glass substrates using ethanolamine and diethanolamine as binders. The sample labeled as S1 was without the supporting layer (FMWCNTs), while groups A and B samples were prepared by solutions containing W-FMWCNTs and UW-FMWCNTs. Table 1 shows the names and specifications of the layers.

The average thicknesses of the layers were estimated to be around 5 μm using the FESEM images of the layer cross-sections. Annealing of the samples was carried out at 150 °C for 5 min. Structural studies and surface morphology of the samples were performed by X-ray diffraction (XRD) (D8advance-Bruker) and field emission scanning electron microscopy (FESEM) (Hitachi S4160), respectively. The optical studies were carried out using a UV–visible spectrometer (Shimadzu 1800).

3. Results and discussion

3.1. Structural characterization

To determine the crystal structure, lattice parameters, average crystallite size, and strain in all samples, XRD patterns of the samples were recorded (Fig. 1).

Table 1
Names and parameters used in each prepared layer.

Name	S1	**Group A (W-FMWNT)**			**Group B (UW-FMWNT)**		
		S2	S3	S4	S5	S6	S7
CIS_2:FMWNT ratio	Without FMWNT	1:0.5	1:1	1:1.5	1:0.5	1:1	1:1.5