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태양전지용 Cu_2S 나노와이어의 제작 및 특성분석

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Copper Sulfide Nanowires for Solar Cells

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Abstract : We fabricated hexagonal copper sulfide (Cu_2S) nanowires to obtain a larger contact area of Cu_2S/CdS solar cell. Copper sulfide nanowires were grown on Cu foil at room temperature by gas-solid reaction. The size, density and shape of nanowires seemed to be affected by the change of reaction time, temperature, crystallographic orientation of Cu foil, and molar ratio of the mixed gas. We controled the length and the diameter of the nanowires and we obtained suitable nanowire arrays which has fitting size for uniform deposition with n-type CdS. CdS layer was deposited on the nanowire array by electrodeposition and it seemed to be uniform. The Cu_2S nanowires/CdS junction showed diode characteristics. A large contact area is expected with the Cu_2S nanowire structure as compared with the Cu_2S thin film.

1. Introduction

One-dimensional nanostructure is very interesting materials because of their distinct application probabilities in physics and optical, electronic, magnetic devices. In photovoltaic cell, one-dimensional nanowire enables us to get a large junction area and short diffusion length of minority carriers to the junction as compared with the case of thin film. So we can expect higher collection efficiency.

In recent years, wiring formed copper sulfide was reported(1) and it has a practical application probability for Cu_2S/CdS solar cells. The Cu_2S/CdS cell is a compound semiconductor. The band gap energy is about 1.2eV and 2.42eV for p-type Cu_2S and n-type CdS, respectively.(2) The stoichiometric Cu_2S chalcocite phase has a high photo absorption coefficient and has long diffusion length above 1μm.(3) The values are suitable for solar energy conversion. The cell is able to be produced very inexpensively and it has also the ease to fabricate on a variety of supporting substrates.

The purpose of this study was to obtain uniform copper sulfide nanowires on copper substrate and fabricate a uniform p-type Cu_2S nanowires/n-type CdS heterojunction for solar cell as illustration in Fig. 1. A wiring formed copper sulfide has relevance to increase its surface area. To obtain copper sulfide nanowires, we used gas-solid reaction.(4) The variables of the process were growth time, temperature, crystallographic orientation of Cu foil and molar ratio of mixed gas. The length and diameter of the copper sulfide nanowires were controlled by the change of the variables. With that, we obtained copper sulfide nanowires with a specific length and the diameter to be a proper contact with n-type materials.

Crystallographic and compositional information was obtained by X-ray diffractometer (XRD) and energy

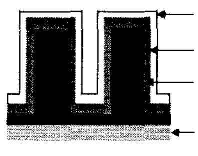

Fig. 1 Illustration for Cu_2S nanowire/CdS structure

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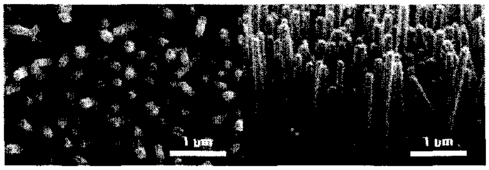


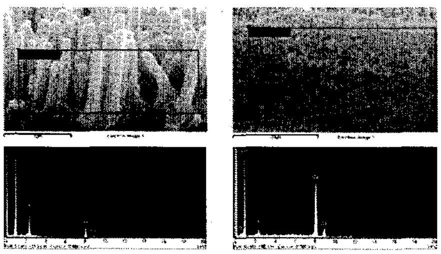
Fig. 2 SEM images of the Cu2S nanowire arrays

dispersive X-ray spectrometer (EDS) measurements. Surface morphology was detected by field-emission scanning electron microscope (FESEM). And electrical properties of a device were analyzed by current-voltage (I-V) measurement.

2. Experimental Procedure

For the growth of copper sulfide nanowires, gas-solid reaction was used on a copper foil at room temperature. The copper foil had 99.98 % purity, 2×1 cm area, 0.25 mm thickness. It was cleaned for 10 min in ultrasonic bath of ethanol to remove organic impurities of the surface, and etched for 30 min in dilute sulfuric acid to reduce the copper oxide layers and to polish the surface chemically. After that, the copper foil was dried by nitrogen gas blowing. As soon as possible, the copper substrate was placed in a reactor filled with nitrogen gas to avoid oxidation of copper. The volume of the mixing chamber and the reactor was 300ml and 600ml, respectively, and it was connected with silicon tube and was blocked off light. And then, a mixture gas consisted of O_2 and H_2S was flowed into the reactor with carrier gas (N_2). Gas injection rate (volume per time) is controlled by mass flow controller (N_2, O_2) and syringe (H_2S). H_2S gas was prepared through a reaction between high purity ZnS and 35% HCl solution. After the gas injection, the reactor was closed. The ratio of the mixture gas was controlled in the range of 1:1~8:1 (O_2/H_2S) and the humidity of the reactor was prevented within the limits of the possible. Total pressure in the reactor was kept at 1 atmosphere.

On the copper sulfide nanowires, a cadmium sulfide layer was grown by electrodeposition.[5] The Electrodeposition bath contained 0.2M $CdSO_4$ and 0.01M $Na_2S_2O_3$. The pH of the solution was adjusted to 4.0. The bath temperature was kept at room temperature. The counter electrode was a platinum and the reference electrode was a saturated calomel electrode. Applied voltage was ± 0.7 V and running time was about 30 second. After that, indium tin oxide (ITO), as a transparent conducting oxide, was grown by RF magnetron sputter.[6]



Element	Weight %	Atomic %
S	17.8	30.15
Cu	82.11	69.85
Totals	100.00	

(a)

Element	Weight %	Atomic %
O	2.83	9.86
S	5.55	9.66
Cu	91.62	80.48
Total	100.00	

(b)

Fig. 3. EDS spectra for (a) the Cu_2S nanowire arrays and (b) the interface between the Cu_2S nanowires and the Cu substrate.

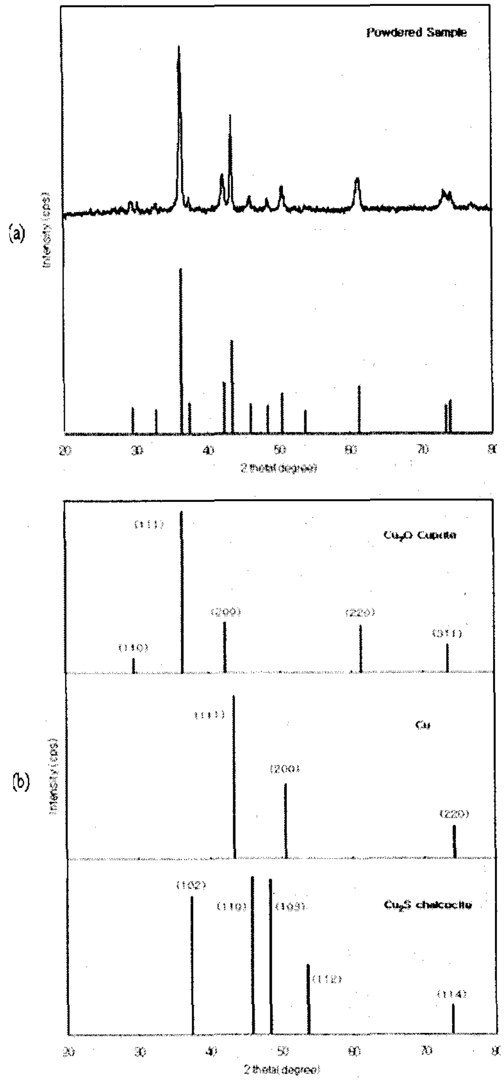


Fig. 4. (a) Powder XRD patterns of the substrate surface after the formation of the Cu_2S nanowires and (b) JCPDS-International Centre for diffraction data of Cu_2O, Cu, Cu_2S.

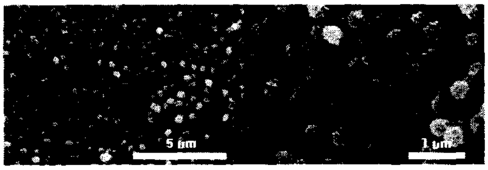


Fig. 5 SEM images of the CdS film on Cu_2S nanowire array.

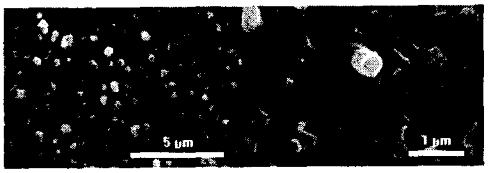


Fig. 7 SEM images of the ITO film on Cu_2S nanowires/CdS structure.

3. Results

By the change of the process variables, we obtained copper sulfide nanowires with the length and diameter of about 1 μm and 100 nm, respectively, and the size and density of the nanowires were comparatively uniform. Refer to Fig. 2 images. The 1 μm is enough distance to absorb solar spectrum in case of Cu_2S.(3) Process variables are as follows. Injection rate of each reactive gas was about 80ml/min and 20ml/min for O_2 and H_2S, respectively. Carrier gas (N_2) was flowed into the reactor with 200ml/min rate. Total injection time was 1 hour. Therefore the molar ratio of mixed gas was 10:4:1 (N_2:O_2:H_2S). Reaction time was 14 hours. Energy dispersive X-ray spectrometer (EDS) analysis in Fig. 3(a) shows that the nanowires were only consisted of copper and sulfur and also shows that the atomic percent ratio of the elements is approximately 2:1. Powdered X-ray diffraction (XRD) pattern in Fig. 4 indicates that the Cu_2S nanowires have chalcocite phase (hexagonal).

Fig. 5 shows that CdS was deposited on the Cu_2S nanowire array by electrodeposition. Thickness of CdS was about 50~100nm and it seems to be uniform. In Fig. 6(c) shows that the CdS has hexagonal structure. And Fig. 7 shows that surface morphology which was made by Cu_2S nanowires was not damaged greatly after annealing and sputtering process. We completed to fabricate Cu/Cu_2S nanowire/CdS/ITO structure. I-V measurement in Fig. 8 shows that the Cu_2S nanowires/CdS structure has rectifying property of p-n junction diode.

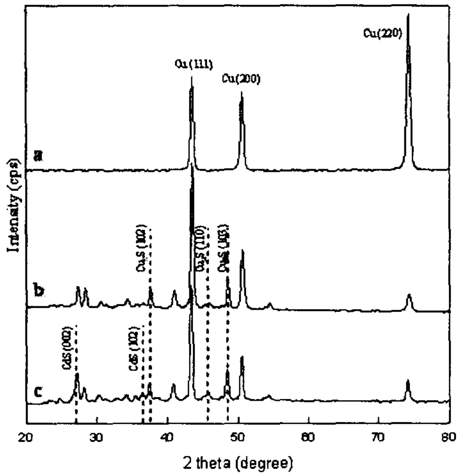


Fig. 6 XRD patterns of (a) Cu, (b) Cu/Cu_2S nanowires, (c) Cu/Cu_2S nanowires/CdS through each stages.

4. Discussion

From a thermodynamic point of view, a standard free energy of formation for Cu_2O and Cu_2S at room temperature is -146 and -86 KJ/mol, respectively.(7) For this reason, copper oxide phase is more stable than copper sulfide phase at room temperature. On the other hand, sulfurization of copper is much faster than that of oxidation. So there is a site competition between sulfur and oxygen atom.(8) There are (111), (200), (220), (311) oriented grains in face-centered cubic (fcc) copper. One of them, (111) oriented grains or grain boundaries are initially to combine with oxygen.(8) Relatively, it was late that oxygen react with (200) and (220) grains. At this time, H_2S has a chance to combine with Cu on (220) or (200) grains. Although copper oxide is more stable phase, therefore, it is possible to grow copper sulfide. In contrast to the film shape of copper oxide, the nucleated copper sulfides grow along the c axis and become a wiring form.(4) XRD patterns in Fig. 6 (a) and (b) exhibit that (200), (220) peaks were greatly decreased by the formation of copper sulfide nanowire.

From EDS spectra in Fig. 3(a), oxygen was not detected on the Cu_2S nanowire arrays, but it remained at the interface between Cu_2S nanowire array and Cu substrate in Fig. 3(b). From powder XRD pattern in Fig. 4, we detected that the structure was consisted of Cu, Cu_2O, Cu_2S. So the oxygen element in the interface related to Cu_2O. Cu_2O is a p-type material and has a 2.0 eV forbidden energy gap.(9) So the final structure was

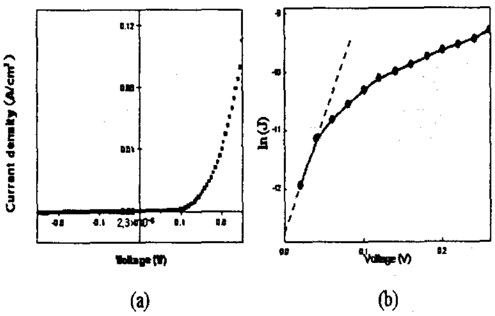


Fig. 8 (a) I-V characteristic of a Cu_2S nanowires /CdS junction and (b) I-V characteristic of a Cu_2S nanowires /CdS junction with the current plotted on a log scale.

partially p-Cu_2O/p-Cu_2S/n-CdS. And the existence of Cu_2O did not greatly affected diode characteristics. To avoid Cu_2O generation is not easy problem because growth of Cu_2S nanowires does not occur without Cu_2O.(4)

By increased junction area, a diffusion distance of minority carriers was reduced. But contact qualities seemed to be worse. By I-V measurement, saturated current density (J_s) of the diode was more than 10^{-5} (A/cm^2). Fig. 8 (b) (the dotted line is ideal diffusion current density when the ideality factor is 1) shows that the series resistance and the recombination current density were too high. Advantages of nanowire structure were canceled by the effect of leakage current, contact resistance, etc.

5. Conclusion

We have successfully grown the copper sulfide nanowires to apply Cu_2S/CdS solar cells. The junction area between p-type Cu_2S and n-type CdS was increased by the formation of nanowires. In this process, we had to control the length, diameter and density of the nanowires for the deposition of n-type materials and for the enough absorption of solar spectrum. Finally, we made the Cu_2S nanowires/CdS structure and the junction showed characteristics of a diode. This work enables us to expect a higher collection efficiency of the solar cell by the increased junction area and by the short diffusion path of the minority carriers to the junction. And our future work is to reduce the leakage current and the contact resistance.

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