The Influence of Doping Ag on Photovoltaic Characteristic of CuI Film

Qiang WANG[1,a], Xi-Ying MA[1,b,*]

[1]School of Mathematics and Physics, Suzhou University of Science and Technology,1# Kerui Road, Suzhou, Jiangsu 215009, China

[a]wangqiang890220@163.com, [b]maxy@mail.usts.edu.cn

*Corresponding author

Keywords: Cuprous Iodide (CuI), Doping Silver (Ag), Photovoltaic Characteristic.

Abstract. Cuprous iodide (CuI) is a p-type semiconductor material with wide band gap, which has attracted considerable attention in recent years because of its unique photoelectric characteristic and potential application in solar cells. This article presents the preparation of Ag doped and undoped CuI films on the substrates of conductive glass by the method of continuous pulling the saturated solution. The influence of dopant Ag on the surface morphology, crystal structure, light absorption and electrical characteristic of CuI thin films were studied. We found that the crystal structure of the CuI films did not change after doped Ag, but the surface morphology of the doped film was better than the undoped film. And the light absorption of the doped CuI film is significantly enhanced. The enhanced absorption of light can improve the photoelectric conversion efficiency of CuI film. In addition, the electrical characteristic of the doped CuI thin film is much better than the undoped film, showing that the doped CuI film can be one as the transport layer material for solar cell.

Introduction

At present, the wide band gap semiconductor thin film material for the potential applications in solar cells has attracted a great deal of attention. Beside a lot of n-type wide band gap materials of CdS, ZnS, ZnSe and In_2S_3[1-4], cuprous iodide (CuI), a p-type material with wide band gap, also caused the researchers' interest. CuI, an I-VII semiconductor material, has three kinds of crystalline phase: α, β, and γ [5-8]. At room temperature, it is p-type wide band gap γ-CuI with zinc-blende structure. Over 390℃, it becomes ionic conductor β-CuI with a wurtzite structure; when temperature is higher than 440℃, it changes to the cubic structure α-CuI of ionic conductor. γ-CuI is a wide band gap semiconductor material with high electrical conductivity [9]. It can be used as a transparent hole-collector in solar cells [10-15]. Since CuI does not produce stress and interface states in the CuI/Si interface [12], it can be inserted into ZnO/Si heterojunction interface to reduce the interface state on the surface of the heterogeneous and improve the heterojunction electric performance. There are many preparation methods of CuI thin film, such as thermal evaporation [12], successive ionic layer adsorption and reaction (SILAR)[15,16], chemical bath deposition [17], electrochemical deposition[18], pulsed laser deposition [19], etc. Those preparation methods, however, are very compulsive. In this paper, we developed a simple operation method with low cost to fast preparation γ-CuI thin film. The principle of the preparation methods comes from the successive ionic layer adsorption and reaction (SILAR). The raw material is the CuI saturated solution with not doping and doping silver (Ag), we insert the substrates into the CuI saturate solution then pull them out, and CuI film is synthesized on the conductive glass substrate at room temperature. Scanning electron microscope (SEM), X-ray diffraction (XRD), UV-3600 spectrophotometer and HMS – 3000 Hall effect instrument were used to study the influence of the surface morphology, crystal structure, light absorption and electrical characteristic of the deposited CuI films.

The Experimental Details

We used the pulling method to deposit the CuI films. First of all, the conductive glass substrates were cleaned using the ultrasonic machine with ethanol and deionized water for 5 mins to remove their surface impurities. CuI and $AgNO_3$ powders with mass ratios of 1:0 or 1:2 were put in a cleaned beaker with 50 ml deionized water and to dissolve under stirring by magnetic stirrers, respectively. This doped or undoped CuI filmS were by inset the conductive glass substrate were put in solution and soaked for 10 s, and then pulled out and cleaned in deionized water for 5 s. The preparation of undoped and doped CuI thin films was completed by 20 times.

Results and Discussion

The Influence of Doping Ag on Absorption

Fig. 1 is the absorption spectra of doped and undoped CuI films, in which the red line is for the doped film and the black line is for the undoped film. Comparing the two curves, we can obviously found that the doped Ag had no effect on the position of absorption peak. The position of absorption peak did not change. And the absorption spectrum did not appear the absorption peak of silver. At the same time, the absorption intensity of CuI thin film was enhanced obviously. So the doped CuI film samples have stronger light absorption, which can improve the photoelectric conversion efficiency of photovoltaic devices based on CuI film.

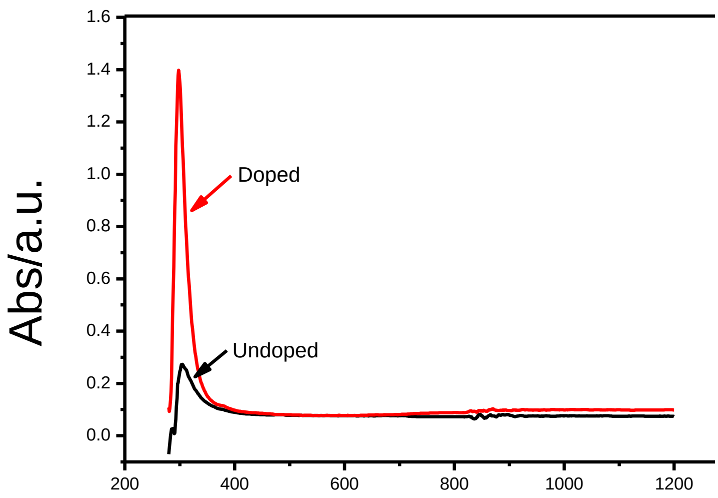

Fig.1 The Absorption Curves of Doped and Undoped CuI Films

The Influence of Doping Ag on X - ray Diffraction (XRD) Image

Using X-ray diffraction, respectively, the crystal structure of the undoped and doped cuprous iodide film was compared and analyzed. As shown in Fig. 2, the red line is for the doped CuI film and the black line is for the undoped film. It can be found that the undoped CuI film did not show an obvious diffraction peak but a lager band, showing it is of a poor crystallinity. The Ag doped sample shows an obvious diffraction peak, showing that the crystallinity of the doped CuI films was obviously enhanced. The intensity of diffraction peak of the doped sample was bigger than the undoped film, showing that the crystallinity of doped CuI film was better. The position diffraction peak is identical with that of the undoped CuI sample, and no other peaks appeared, showing that other silver mater was no formed and the doped silver did not change the crystal structure of CuI.

By the analysis of the XRD images of the undoped and doped CuI film, it can be found that doped silver had played a catalytic role on the growth of thin films. The crystallinity of thin film had very big enhancement and there is no introduction of diffraction peaks of silver.

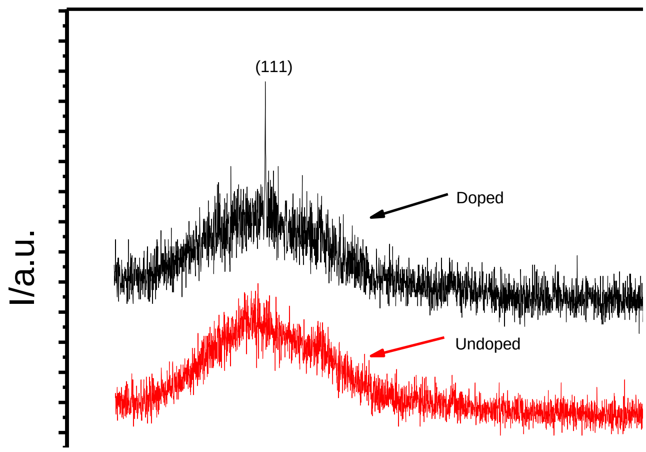

Fig.2 The XRD of the undoped and doped CuI films

The Influence of Doping Ag on the Electrical Characteristics

Using HMS - 3000 Hall effect instrument, we measured the *I-V* curves of the cuprous iodide film surface, as shown in Fig. 3.The *I-V* curves of undoped CuI films were not very smooth, and appeared some waves. It showed that the surface of films we prepared is not smooth. This was what we need to further improve. On the contrary, the doped film shows a relatively smooth *I-V* curve, showing that the doped CuI film has good crystallinity, and the quality of the film has improved.

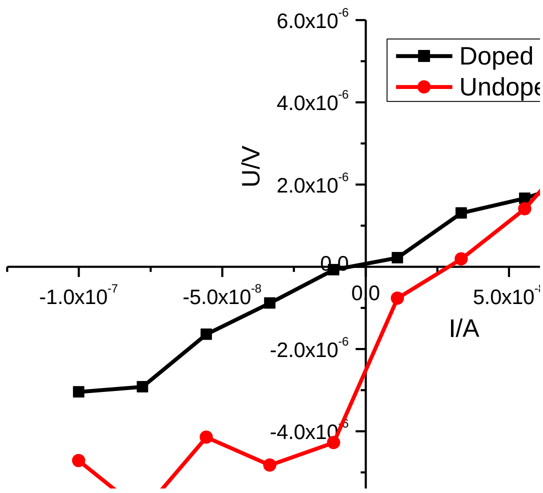

Fig.3 The *I-V* Curves of the Undoped and Doped CuI Films

The Influence of Doping Ag on Scanning Electron Microscope (SEM) Image

The surface morphology of undoped and doped cuprous iodide films was measured by means of scanning electron microscope (SEM), as shown in Fig. 4. Figure (a) and figure (b) were the SEM images of undoped and doped of CuI films respectively. It can be obviously found that the surface morphology of undoped CuI film was not smooth, and there were some heterogeneous places. By the contrast, the surface morphology of the doped CuI film was much smoother, and the particles were much more uniform. So the quality of the film had been enhanced obviously. In addition, the surface of doped CuI thin film was much smoother and has better electrical characteristic, so the CuI film can be the better one as the transport layer material for solar cell.

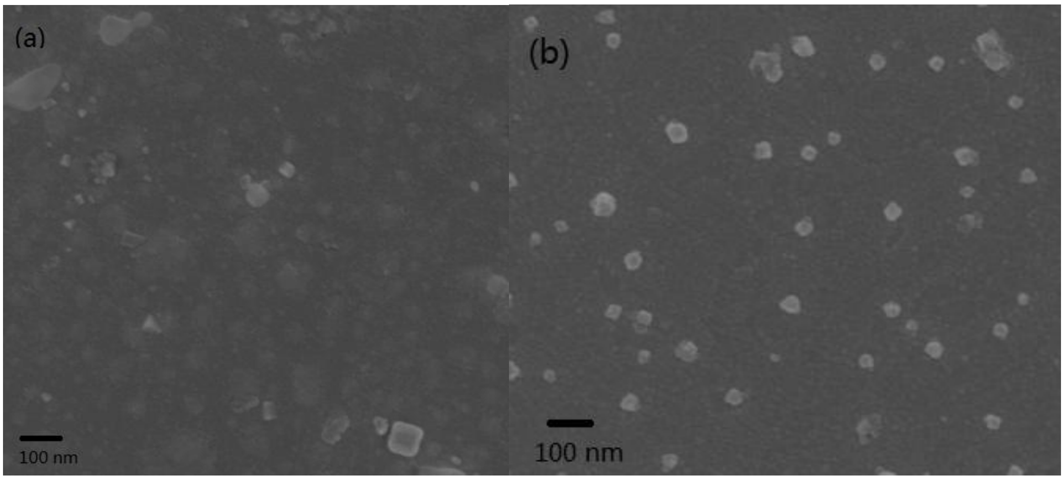

Fig.4 The SEM of the Undoped and Doped CuI Films

Summary

We adopt the method of continuous pulling to form CuI of film at room temperature. With undoped and doped CuI saturated solution as raw material, CuI film is synthesized on conductive glass substrate. Using scanning electron microscope (SEM), X-ray diffraction (XRD), UV - 3600 spectrophotometer, HMS – 3000 Hall effect instrument to study the effect of doping silver on surface morphology, crystal structure, light absorption and electrical characteristic of cuprous iodide film. We found that the surface morphology of CuI film is much smoother after doping Ag. The light absorption and electrical characteristic had increased significantly. The crystallinity of CuI film had very big enhancement. Therefore, Ag has played a catalytic role on the growth of CuI films. The doped CuI film samples have stronger light absorption, which can significantly increase the applications of the semiconductor photovoltaic device based on CuI film. It provides the future experiment with a new solution for the preparation of high purity cuprous iodide film.

Acknowledgement

This work was supported in part by the National Natural Science Foundation of China (No. 60976071), the Innovation Program for Postgraduate of Jiangsu Province (No.KYLX_1285) and the Innovation Program for Postgraduate of Suzhou University of Science and Technology (No. SKCX14_061).

Reference

[1] M.A. Contreras, M.J. Romero, B. To, F. Hasoon, R. Noufi, S. Ward, and K. Ramanathan, Optimization of CBD CdS process in high-efficiency Cu(In,Ga)Se_2-based solar cells, J. Thin Solid Films. 403 (2002) 204-211.

[2] A. Ennaoui, W. Eisele, M. Lux-Steiner, T.P. Niesen, E. Karg, Highly efficient Cu(Ga,In)(S,Se)(2) thin film solar cells with zinc-compound buffer layers, J. Thin Solid Films. 431(2003) 335-339.

[3] A. Ennaoui, S. Siebentritt, M.C. Lux-Steiner, et al, High-efficiency Cd-free CIGSS thin-film solar cells with solution grown zinc compound buffer layers, J. Solar Energy Materials and Solar Cells. 67(2001) 31-40.

[4] S. Spiering, A. Eicke, D. Hariskos, M. Powalla, N. Naghavi, D. Lincot, Large-area Cd-free CIGS solar modules with In2S3 buffer layer deposited by ALCVD, J. Thin Solid Films. 451(2004) 562-566.

[5] J.X.M. Zheng-Johansson, R.L. McGreevy, A molecular dynamics study of ionic conduction in CuI. II. Local ionic motion and conduction mechanisms, J. Solid State Ionics. 83 (1996) 35-48.

[6] J.X.M. Zheng-Johansson, I. Ebbsjo, R.L. McGreevy, A molecular dynamics study of ionic conduction in CuI. I. Derivation of the interionic potential from dynamic properties, J. Solid State Ionics.82 (1995) 115-122.

[7] S. Miyake, S. Hoshino, T. Takenaka, On the phase transition in cuprous iodide, J. Journal of the Physical Society of Japan. 7 (1952) 19-24.

[8] W. Buhrer, W. Halg, Crystal structure of high-temperature cuprous iodide and cuprous bromide, J. Electrochimica Acta. 22 (1977) 701-704.

[9] I. Konovalov, R. Szargan, Valence band alignment with a small spike at the $CuI/CuInS_2$ interface, J. Applied Physics Letters. 82.13(2003) 2088-2090.

[10]J.A. Christians, R.C.M. Fung, P.V. Kamat, An inorganic hole-conductor for organo-lead halide perovskite solar cells. Improved hole conductivity with copper iodide, J. Journal of the American Chemical Society. 136.2(2013) 758-764.

[11]A.R. Zainun, M.H. Mamat, U.M. Noor, et al, Particles size and conductivity study of P-Type copper (I) iodide (CuI) thin film for solid state dye-sensitized solar cells, C. Materials Science and Engineering. 17(2011) 012009(1-7).

[12]H. Iimori, S. Yamane, T. Kitamura, et al, High photovoltage generation at minority-carrier controlled n-Si/p-CuI heterojunction with morphologically soft CuI, J. The Journal of Physical Chemistry C. 112.30(2008) 11586-11590.

[13]I. Konovalov, L. Makhova, L. Roussak, CuI/Zn_{2x} (CuIn) $_{1-x}S_2/AgIn_5S_8$ double heterojunction solar cells, J. physica status solidi (a). 206.5(2009) 1067-1071.

[14]I. Konovalov, L. Makhova, Valence band offset at interfaces between CuI and indium sulfides, J. Journal of Applied Physics. 103.10(2008) 103702(1-7).

[15]B.R. Sankapal, A. Ennaoui, T. Guminskaya, et al, Characterization of p-CuI prepared by the SILAR technique on Cu-tape/n-CuInS2for solar cells, J. Thin Solid Films. 480(2005) 142-146.

[16]S.L. Dhere, S.S. Latthe, C. Kappenstein, et al, Comparative studies on p-type CuI grown on glass and copper substrate by SILAR method, J. Applied Surface Science. 256.12(2010) 3967-3971.

[17]B.R. Sankapal, E. Goncalves, A. Ennaoui, et al, Wide band gap p-type windows by CBD and SILAR methods, J. Thin Solid Films. 451(2004) 128-132.

[18]H. Kang, R. Liu, K. Chen, et al, Electrodeposition and optical properties of highly oriented γ-CuI thin films, J. Electrochimica Acta. 55.27(2010) 8121-8125.

[19]B.L. Zhu, X.Z. Zhao, Transparent conductive CuI thin films prepared by pulsed laser deposition, J. physica status solidi (a). 2011, 208.1(2011) 91-96.