第29卷　第5期
2008年5月

半　导　体　学　报
JOURNAL OF SEMICONDUCTORS

Vol.29　No.5
May,2008

Doped-Chamber Deposition of Intrinsic Microcrystalline Silicon Thin Films and Its Application in Solar Cells*

Sun Fuhe, Zhang Xiaodan†, Zhao Ying, Wang Shifeng, Han Xiaoyan, Li Guijun, Wei Changchun, Sun Jian, Hou Guofu, Zhang Dekun, Geng Xinhua, and Xiong Shaozhen

(Institute of Photo-Electronics Thin Film Devices and Technique, Nankai University, Tianjin 300071, China)
(Key Laboratory of Photo-Electronics Thin Film Devices and Technique of Tianjin, Tianjin 300071, China)
(Key Laboratory of Opto-Electronic Information Science and Technology (Nankai University, Tianjin University), Ministry of Education, Tianjin 300071, China)

Abstract: A series of microcrystalline silicon thin films were fabricated by very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) at different silane concentrations in a P chamber. Through analysis of the structural and electrical properties of these materials, we conclude that the photosensitivity slightly decreased then increased as the silane concentration increased, while the crystalline volume fraction indicates the opposite change. Results of XRD indicate that thin films have a (220) preferable orientation under certain conditions. Microcrystalline silicon solar cells with conversion efficiency 4.7% and micromorph tandem solar cells 8.5% were fabricated by VHF-PECVD (p layer and i layer of microcrystalline silicon solar cells were deposited in P chamber), respectively.

Key words: VHF-PECVD; intrinsic microcrystalline silicon; solar cells
PACC: 8115H
CLC number: TN304.1　　**Document code:** A　　**Article ID:** 0253-4177(2008)05-0855-04

1 Introduction

Microcrystalline silicon (μc-Si:H) thin films are of great interest for their potential applications in solar cells due to their low apparent band gap, high stability, and low process cost[1,2]. The preparation and characteristic research of μc-Si:H solar cells have become a hot topic in the field of PV devices[3,4].

High efficiency amorphous silicon solar cells have been fabricated in a single chamber reactor by the IMT group *et al*.[5~7]. However, most μc-Si:H solar cells are prepared in sophisticated, multi-chamber, loadlocked deposition systems, which enhances process cost and consumes time[5,6]. To promote the industrialization of μc-Si:H solar cells, the ideal solution would be to combine a low cost single-chamber reactor with a process technology of a-Si:H cells.

Recently, Li *et al*. have deposited a highly stable μc-Si:H p-i-n single junction solar cell of ~6.5% efficiency, in a single chamber reactor using seeding methods[8]. However, there has been no study of single-chamber deposition of μc-Si:H solar cells in China. In this paper, a series of μc-Si:H thin films were fabricated in a P chamber by VHF-PECVD. Then, the effect of silane concentration on the growth of the films was investigated. Finally, μc-Si:H solar cells and micromorph tandem solar cells were fabricated by VHF-PECVD (p-layer and i-layer of μc-Si:H solar cells were deposited in P chamber).

2 Experimental details

Microcrystalline silicon thin films and solar cells (p-layer and i-layer) were prepared in the P chamber of a cluster CVD system[9] at an excitation frequency of 60MHz. The n-layer was deposited in the N chamber by the RF-PECVD method (13.56MHz). The intrinsic films were grown on Eagle2000 glass treated by HF (5%). The pressure of the source gas was kept at 120Pa. The silane concentration ($SC = [SiH_4]/[SiH_4 + H_2]$) varied from 4% to 7% at the power of 20W. The structure of the single junction solar cell was ZnO/p(μc-Si:H)/i(μc-Si:H)/n(a-Si:H)/ZnO/Ag.

The photo/dark conductivity was measured with an aluminum coplanar contact at room temperature using a Keithley 617 and the Raman scattering experiment was performed using a 632.8nm He-Ne laser.

---

* Project supported by the National High Technology Research and Development Program of China (No.2007AA05Z436), the State Key Development Program for Basic Research of China (Nos.2006CB202602, 2006CB202603), the National Natural Science Foundation of China (No.60506003), the Starting Project of Nankai University (No.J02031), the International Cooperation Project between China-Greece Government (No.2006DFA62390), and the Program for New Century Excellent Talents in University of China (NCET)

† Corresponding author. Email: xdzhang@nankai.edu.cn

Received 30 August 2007, revised manuscript received 5 October 2007

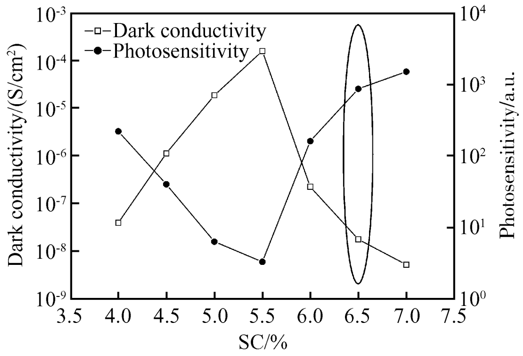

Fig. 1 Dark conductivity and photosensitivity of films prepared at different silane concentrations

The crystalline volume fraction (X_c) described the crystallinity of the films:

$$X_c = (I_{510} + I_{520})/(I_{480} + I_{510} + I_{520})^{[10]} \quad (1)$$

In addition, X-ray diffraction using a Cu-Kα radiation source was also applied for the characterization of the structural variation of the films. *I-V* characteristics of the solar cells were measured under illumination with an AM 1.5 (100mW/cm^2) solar condition.

3 Results and discussion

As has been reported, a high quality μc-Si:H i layer is the key factor for high efficiency solar cells. First, intrinsic films prepared at different silane concentrations have been studied. Figure 1 shows the dark conductivity and photosensitivity of films as a function of silane concentrations. The photosensitivity slightly decreases then increases as the silane concentration increases, while the conductivity indicates the opposite change.

The structural properties of thin films have a close relationship to their electrical properties. Raman scattering spectra is an effective means to characterize the structural properties of thin films[11]. The Raman scattering spectra of silicon films deposited at different SCs are compared in Fig. 2. The peak intensity of c-Si at 520cm^{-1} slightly increases then decreases as the SC increases. The peak near 480cm^{-1} is dominant at SC of 7%, which suggests a decrease of the microcrystalline phase and an increase of the amorphous phase. Figures 1 and 2 show that the decrease in X_c is accompanied by an increase in the photosensitivity as SC increases from 5.5% to 7%. This is because the atomic hydrogen to silane radical ratio decreases as SC increases, and the thin films show amorphous characteristics. For the films prepared with SC between 4% and 5.5%, the X_c increases, but the corresponding photosensitivity decreases. A possible reason is that the material's deposition time is 40min, so the lower silane concentration or the stronger hydrogen dilution, the lower the growth rate. The thickness measurement of the thin films reveals this. Furthermore, microcrystalline silicon thin films usually exhibit non-uniformity along the growth direction[12]. Therefore, the ultra thin film shows low crystalline volume fraction.

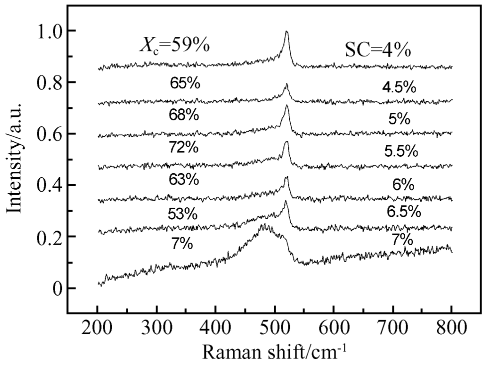

Fig. 2 Raman results of films prepared at different silane concentrations

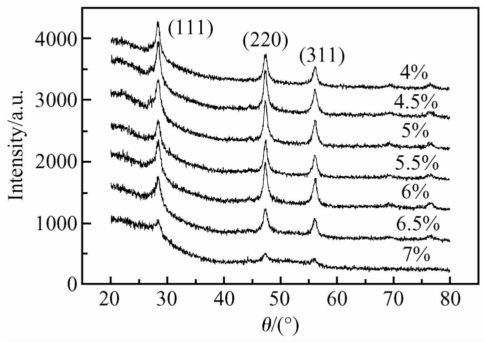

Fig. 3 XRD profiles of films prepared at different silane concentrations (GI-XRD)

To further study the quality of the films, X-ray diffraction spectra analysis was carried out. As can be seen from Fig. 3, all the films show the crystallization information, which is consistent with the above Raman results. Although the thin film prepared at SC of 6% demonstrates the (220) orientation intensity enhancement, the other films are not very evident. Here, we use another kind of XRD measurement mode[13] (Fig. 4). Thin films deposited at SC from 4.5% to 6.5% have a (220) preferable orientation, which is important to enhance the short circuit current of solar cells[14,15].

To determine whether these high-quality μc-Si:H films are necessary for the application of solar cell, we first selected the film with (220) preferred orientation for the application in solar cells. This film was prepared at an SC of 6.5%, and the activation energy and X_c of materials were 0.52eV, and 53%, respectively. A microcrystalline silicon p-i-n solar cell with a conversion efficiency of 4.7% was deposited by

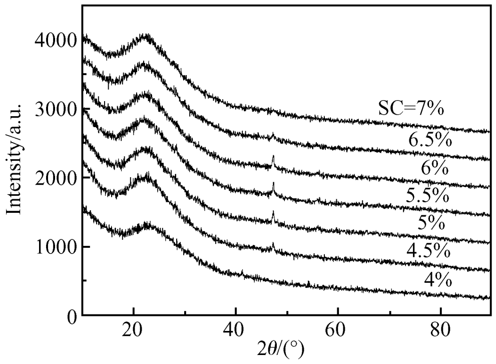

Fig. 4 XRD profiles of films prepared at different silane concentrations (θ/θ-XRD)

VHF-PECVD (p-layer and i-layer in P chamber, n-layer in N chamber). Figure 5 shows the *J-V* performance of the cell (J_{sc} = 17.25mA/cm^2, V_{oc} = 0.469V, FF = 0.58). J_{sc} and FF are not very high, which means that the cell has a relatively high series resistance, lower shunt resistance, and poor interface characteristics, mainly a p/i interface without processing treatment. The p-layer is a boron-doped silicon thin film deposited by plasma in a gas mixture containing silane and diborane gas. The boron from the reactor walls, pumping lines, or the layer itself can contaminate the intrinsic i-layer at the critical p-i interface. Then, it weaks the strength of the built-in electrical field close to the p-i interface, which may also reduce the electron life time. This provokes a less efficient carrier separation in this zone and leads to a reduced collection efficiency in the solar cell[7,16]. Thus, taking effective measures to avoid boron contamination is important.

Various techniques to reduce or eliminate the boron contamination in the subsequent i-layer have been investigated for a-Si:H solar cells, such as long time pumping or the flushing method. In particular, the latter has more applications, including NF_3 gas flush[7], hydrogen plasma[17] or CO_2 plasma[18], water vapor treatment[5], or ammonia flush[19]. Therefore, in order to further improve the performance of microcrystalline silicon solar cells, we will pay attention to the appropriate techniques to deal with boron contamination at the p/i interface in subsequent experiments.

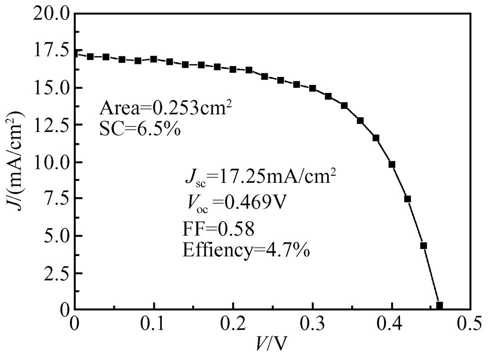

Fig. 5 Photo *J-V* curve of single junction microcrystalline silicon solar cells

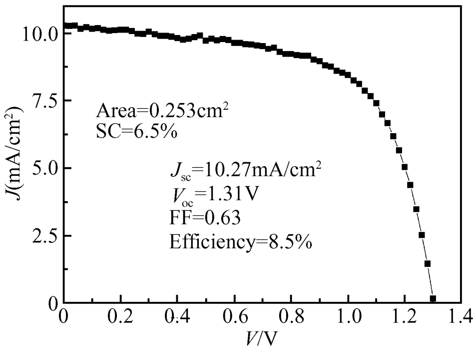

Fig. 6 Photo *J-V* curve of micromorph tandem solar cells

In addition, a-Si:H/μc-Si:H tandem cells under the same process condition were also prepared. Figure 6 gives the *J-V* characteristics of the tandem cells with a conversion efficiency of 8.5%.

4 Conclusion

The properties of μc-Si:H thin films prepared at different SCs in a P chamber by VHF-PECVD were investigated. The results of XRD measurements show thin films have a (220) preferable orientation under certain SC conditions. Meanwhile, the results of dark conductivity (1.7×10^{-8} S/cm), photosensitivity (900), activation energy (0.52eV), and X_c(53%) of thin films also indicate that device grade microcrystalline silicon film has been deposited at an SC of 6.5%. Finally, microcrystalline silicon solar cells with 4.7% conversion efficiency, and a-Si:H/μc-Si:H tandem solar cells with 8.5% conversion efficiency were fabricated by VHF-PECVD (p layer and i layer of microcrystalline silicon solar cells were deposited in P chamber), respectively.

References

[1] Meier J, Dubail S, Golay S, et al. Microcrystalline silicon and the impact on micromorph tandem solar cells. Solar Energy Materials and Solar Cells, 2002, 74: 457

[2] Rech B, Kluth O, Repmann T, et al. New materials and deposition techniques for highly efficient silicon thin film solar cells. Solar Energy Materials and Solar Cells, 2002, 74: 43

[3] Shah A, Meier J, Vallat-Sauvain E, et al. Microcrystalline silicon and 'micro-morph' tandem solar cells. Thin Solid Films, 2002, 403/404: 179

[4] Strahm B, Howling A A, Sansonnens L, et al. Microcrystalline silicon deposited at high rate on large areas from pure silane with efficient gas utilization. Solar Energy Materials and Solar Cells, 2007, 91: 495

[5] Kroll U, Bucher C, Benagli S, et al. High-efficiency p-i-n a-Si:H solar cells with low boron cross contamination prepared in a large-

area single-chamber PECVD reactor. Thin Solid Films，2004，451/452：525

[6] Platz R，Fischer D，Dubail S，et al. a-Si：H/a-Si：H stacked cell from VHF-deposition in a single chamber reactor with 9% stabilized efficiency. Solar Energy Materials and Solar Cells，1997，46：157

[7] Catalano A，Wood G. A method for improved short wavelength response in hydrogenated amorphous silicon based solar cells. J Appl Phys，1988，63(4)：1220

[8] Li Y M，Anna J A，Foustotchenko S A，et al. Some observations on seeing and stability of nc-Si solar cells. IEEE Photovoltaic Specialists Conference，2005：1420

[9] Zhao Ying，Zhang Xiaodan，Zhu Feng，et al. Fabrication of high efficiency a-Si：H/μc-Si：H tandem solar cell modules. 15th International Photovoltaic Science & Engineering Conference (PVSEC-15) Shanghai，China，2005：65

[10] Droz C，Vallat-Sauvain E，Bailat J，et al. Application of Raman spectroscopy for the microstructure characterization in microcrystalline silicon solar cells. 17th European Photovoltaic Solar Energy Conference Munich，Germany，2001：2917

[11] Zhang Xiaodan，Gao Yantao，Zhao Ying，et al. Fabrication of microcrystalline silicon materials and microcrystalline silicon solar cells and study on their properties. Journal of Synthetic Crystals，2005，34：298(in Chinese)[张晓丹，高艳涛，赵颖，等. 本征微晶硅薄膜和微晶硅电池的制备及其特性研究. 人工晶体学报，2005，34：298]

[12] Zhang Xiaodan，Zhao Ying，Zhu Feng，et al. Study of vertical non-uniformity of microcrystalline silicon thin film using Raman spectra and AFM. Journal of Synthetic Crystals，2004，33(6)：960(in Chinese)[张晓丹，赵颖，朱锋，等. 微晶硅薄膜纵向不均匀性的 Raman 光谱和 AFM 研究. 人工晶体学报，2004，33(6)：960]

[13] Zhang Xiaodan，Gao Yantao，Zhao Ying，et al. Fabrication of microcrystalline silicon thin film and the X-ray of its microstructure. Annual Symposium of China Solar Energy，2004：750 (in Chinese)[张晓丹，高艳涛，赵颖，等. 微晶硅薄膜的制备及其结构的 X-Ray 衍射分析. 2004 年中国太阳能学会学术年会，2004：750]

[14] Torres P，Meier J，Kroll U，et al. Fast deposition of μc-Si：H by restrictive dilution and enhanced HF-power. Twenty Sixth IEEE Photovoltaic Specialists Conference，1997：711

[15] Keppner H，Meier J，Torres P，et al. Microcrystalline silicon and micromorph tandem solar cells. Appl Phys Lett，1999，69：169

[16] Lee S C. Boron contamination in the intrinsic layers of amorphous silicon solar cells. J Appl Phys，1984，55(12)：4426

[17] Tsuo Y S，Xu Y，Crandall R S. Hydrogen-plasma reactive flushing for a-Si：H PIN solar cell fabrication. Mater Res Soc Symp，1989，149：471

[18] Platz R，Fischer D，Dubail S，et al. a-Si：H/a-Si：H stacked cell from VHF-deposition in a single chamber reactor with 9% stabilized efficiency. Solar Energy Materials & Solar Cells，1997，46：157

[19] Ballutaud J，Bucher C，Hollenstein C H，et al. Reduction of the boron cross-contamination for plasma deposition of p-i-n devices in a single-chamber large area radio-frequency reactor. Thin Solid Films，2004，468：222

掺杂室沉积本征微晶硅材料及其在太阳能电池中的应用*

孙福河　张晓丹†　赵　颖　王世峰　韩晓艳　李贵军　魏长春　孙　建
侯国付　张德坤　耿新华　熊绍珍

(南开大学光电子薄膜器件与技术研究所，天津　300071)
(南开大学光电子薄膜器件与技术天津市重点实验室，天津　300071)
(光电信息技术科学教育部重点实验室(南开大学，天津大学)，天津　300071)

摘要： 在掺杂 P 室采用甚高频等离子体增强化学气相沉积(VHF-PECVD)技术，制备了不同硅烷浓度条件下的本征微晶硅薄膜. 对薄膜电学特性和结构特性的测试结果分析表明：随硅烷浓度的增加，材料的光敏性先略微降低后提高，而晶化率的变化趋势与之相反；X 射线衍射(XRD)测试表明材料具有(220)择优晶向. 在 P 腔室中用 VHF-PECVD 方法制备单结微晶硅太阳能电池的 i 层和 p 层，其光电转换效率为 4.7%，非晶硅/微晶硅叠层电池(底电池的 p 层和 i 层在 P 室沉积)的效率达 8.5%.

关键词： 甚高频等离子体增强化学气相沉积；本征微晶硅；太阳能电池

PACC： 8115H

中图分类号： TN304.1　　**文献标识码：** A　　**文章编号：** 0253-4177(2008)05-0855-04

---

* 国家高技术研究发展规划(批准号：2007AA05Z436)，国家重点基础研究发展规划(批准号：2006CB202602，2006CB202603)，国家自然科学基金(批准号：60506003)，南开大学博士启动基金(批准号：J02031)以及科技部国际合作重点项目(批准号：2006DFA62390)和教育部新世纪人才计划资助项目

† 通信作者. Email：xdzhang@nankai.edu.cn

2007-08-30 收到，2007-10-05 定稿