第23卷第9期　　半　导　体　学　报　　Vol.23, No.9
2002年9月　　CHINESE JOURNAL OF SEMICONDUCTORS　　Sep., 2002

Fabrication of Hydrogenated Microcrystalline Silicon Thin Films at Low Temperature by VHF-PECVD*

Yang Huidong[1,2], Wu Chunya[1], Mai Yaohua[1], Li Hongbo[1], Xue Junming[1], Li Yan[1],
Ren Huizhi[1], Zhang Lizhu[3], Geng Xinhua[1] and Xiong Shaozhen[1]

(1 *Institute of Photoelectronics, Nankai University, Tianjin* 300071, *China*)
(2 *Institute of Thin Films and Nano-Materials, Wuyi University, Jiangmen* 529020, *China*)
(3 *Tianjin School of Mechanical and Electrical Industry, Tianjin* 300071, *China*)

Abstract: Using H_2-diluted silane, series of μc-Si:H films are fabricated at low temperature with VHF-PECVD. The thickness measurements reveal that the deposition rates are obviously enhanced with higher plasma excitation frequency or working pressure, but increase firstly and then decrease with the increase of plasma power density. Raman spectra show that the crystallinity and the average grain sizes of the films strongly depend on the temperature of substrate and the concentration of silane. However, the plasma excitation frequency only has effect on the crystallinity, and a maximum occurs during the further increase of plasma excitation frequency. From XRD and TEM experiments, three preferential crystalline orientations (111), (220) and (311) are observed, and the average grain sizes are different for every crystalline orientation.

Key words: μc-Si:H thin films; VHF-PECVD; deposition rate; crystallinity
PACC: 7360F; 7280N; 8115H
CLC number: TN304.055　　**Document code:** A　　**Article ID:** 0253-4177(2002)09-0902-07

1 Introduction

In recent years, more and more attentions have been paid to hydrogenated microcrystalline silicon (μc-Si:H) film deposited at low temperature because of its promising application to stable high efficiency solar cells[1~3], and a large potential to be applied to thin film transistors and color sensors[4,5] to replace polycrystalline silicon films formed by high temperature deposition techniques. Since μc-Si:H has an indirect band gap, when using as a solar cell active material, its thickness usually should be more than 2μm for sufficient absorption of sun light even using optical trapping technique[3]. However, the deposition rate of μc-Si:H fabricated with conventional RF-PECVD is generally much lower than that of hydrogenated amorphous silicon (a-Si:H). In order to increase the deposition rate of μc-Si:H, techniques such as hot wire (HW), electron cyclotron resonance (ECR) and very high frequency plasma-enhanced chemical

---

* Project supported by the Development Plan of the State Key Fundamental Research of China (Grant Nos. G2000028202 and G2000028203)

Yang Huidong　male, was born in 1967, associate professor and PhD candidate. He is engaged in the research on semiconductor thin film materials and devices.

Wu Chunya　female, was born in 1969, associate professor and PhD. She is engaged in theoretical research on opto-electrical materials and devices.

Xiong Shaozhen　female, was born in 1939, professor and tutor of PhD candidates. She is engaged in the research on semiconductor devices and opto-electric technology.

Received 18 January 2002, revised manuscript received 8 April 2002

vapor deposition (VHF-PECVD) have been successfully adopted[6~8]. Among these methods, the VHF-PECVD technique is the most common used because of its being compatible with the well-established a-Si:H films technology. So far, many research groups have made great progress in the study of μc-Si:H films deposited by VHF-PECVD technique[9~12].

To our knowledge, investigations on μc-Si:H films fabricated by VHF-PECVD technique have never been reported by Chinese researchers before, though there were some previous works about nanometer crystalline silicon or μc-Si:H/a-Si:H multilayers fabricated by RF-PECVD technique[13,14]. In this paper, investigations on μc-Si:H films fabricated at a low temperature with VHF-PECVD have been presented. The results indicate that VHF-PECVD technique can effectively lower the deposition temperature and enhance the deposition rates of μc-Si:H films, which implies that VHF-PECVD will play an important role in the high deposition rate growth of μc-Si:H films at the low temperature.

2 Experiments

All the films investigated here were deposited on general optical glass in a capacitive-coupled VHF-PECVD system. The plasma excitation frequencies (ν) were in the range of 60~90MHz. The base vacuum was approximately 1×10^{-4} Pa. The dilution ratio ($S_c = SiH_4/(SiH_4 + H_2)$) was adjusted by gas flux and working pressure (p_g) which was controlled by pump rate and gas flux. Different μc-Si:H films were deposited by varying deposition conditions. The thickness of μc-Si:H films was obtained from the optical transmission and reflection (T & R) spectra measured by optical multichannel analysis-OMA (EG&G). Then the deposition rates were calculated through the films thickness divided by the corresponding deposition time. The structural properties of the μc-Si:H films were characterized using Raman scattering spectroscopy (Micro-Raman scope MKI2000, Renishaw) with resolution less than 1cm^{-1}, X-ray diffraction (XRD, Rigaku D/MAX 2500), transmission electron microscope (TEM) and selected area electron diffraction (SAED). For TEM and SAED measurement, EM-400ST Philips was operated at ×57000 for the dark-field image and with the acceleration voltage of 100kV for the SAED.

3 Results and discussions

3.1 Deposition rates

In order to investigate the effects of deposition conditions on the deposition rates, three different series of thin films were deposited with different gas pressures (p_g), different plasma power density (P_d) and different excitation frequency (ν) of VHF-PECVD. The deposition rates varied with the corresponding deposition conditions were shown in Fig.1(a), (b) and (c), respectively.

Figure 1(a) shows the deposition rates of μc-Si:H films as a function of the plasma excitation frequency. It can be seen that the deposition rates are much higher than those prepared by RF-PECVD technique and increased from 0.74nm/s to 1.3nm/s as increasing the plasma excitation frequency from 60MHz to 90MHz. Comparing to the RF-PECVD, the VHF plasma having lower electron temperature and higher electron density provides sufficient source of favorable gas phase reactive species which is required to obtain a fast growth of crystalline material. As proved previously[15], high frequency plasma can enhance dissociation of silane in the bulk plasma, reduce the thickness of plasma sheath, namely low ion energy. Thus an increased radical density (such as hydrogen and SiH_x precursors) can be prone to help them traverse the sheath and reach the growing surface of the film, thereby improve the deposition rate. The high density of H^* radicals required by effective selective etching to the disordered Si-bond is also beneficial to obtain μc-Si:H film. In addition, comparing to the previous work, no maximum deposition rate was observed here during the change of plasma excitation frequency in the same range as they used. This disagreement implies that the growth process of μc-Si:H films strongly depends on the deposition system.

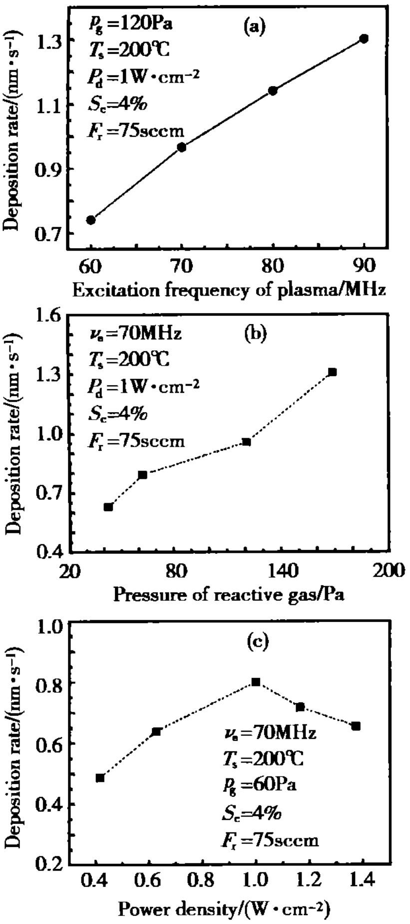

Fig. 1 Dependence of deposition rate on excitation frequency of plasma (a), pressure of working gases (b), and power density of plasma (c)

From Fig. 1 (b), the deposition rates of μc-Si:H films obviously increase with the pressure p_g and can be reached to about 1.4nm/s at p_g = 170Pa. As well known, higher working gas pressure means there are higher concentration of reactive radicals. Guo *et al*.[16] have ever proposed a novel high-pressure depletion (HPD) method in their RF-PECVD system and the deposition rate can reach 0.93nm/s at 350℃. Recently, the combination of HDP method with VHF plasma has been sucessfully developed[17,18].

Figure 1(c) shows the deposition rate as a function of the discharge power density. An abnormal result can be observed clearly. The deposition rate increases in the lower power density range and reaches a maximum around the power density of 1W/cm^2, then it decreases with the further increasing of power density. This can be explained by the enhanced bombardment effect at higher power density of plasma, but the essential cause needs to be further investigated. Some valuable results have also been obtained by the optical emission spectroscopy, which will be reported elsewhere.

3.2 Raman scattering

The change in the Raman spectra with the increase of T_s, S_c and ν are shown in Fig. 2 (a), (b) and (c), respectively. As described in detail by previous work[9], the results of Raman spectra can provide two parameters, the crystallinity (X_c) and the average grain size (d), to characterize the structural properties of samples.

From Fig. 2 (a), the transition from amorphous phase to crystalline phase with different T_s can be observed. The transition temperature occurred at nearly T_s = 150℃, that is to say, the utilization of VHF plasma can effectively lower the formation temperature of μc-Si:H films. Furthermore, the crystallinity X_c and the average grain size d increased with the increase of T_s are also well observed. Figure 2 (b) reveals the similar transition as shown in Fig. 2 (a), but the crystallinity X_c and the average grain size d are decreased with the increase of silane diluted concentration and the transition approximately occurs at S_c = 6%～8%. Figure 2(c) directly shows the influence of plasma excitation frequency on the Raman spectra. Obviously, when the plasma excitation frequency varying from 60MHz to 90MHz, all the deposited films have the uniform average grain size d(～8.4nm), the crystallinity X_c increases from 60MHz to 80MHz and arrives at a maximum at 80MHz (～65%), then begins to decrease appreciably between

80MHz and 90MHz. Such a result clearly indicates that the VHF plasma should not be taken as the only factor for fabricating the device quality μc-Si:H thin film at both low temperature and high deposition rate. Usually, the deposition conditions need to be optimized and the optimum conditions are generally different for different deposition systems. So it is important to understand the growth mechanism of μc-Si:H film, despite many efforts have been made. It is still ongoing work waiting for further investigation.

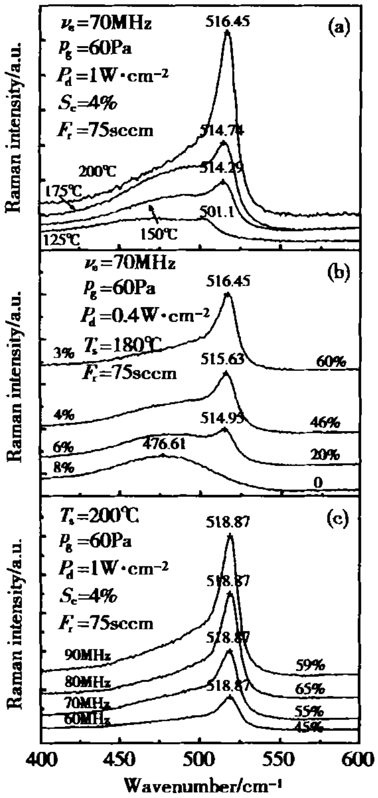

Fig.2 Raman spectra with temperature of substrate T_s(a), diluted concentration of silane S_c(b) and excitation frequency (c)

3.3 XRD, TEM and SAED

The X-ray diffraction results of samples deposited with different plasma excitation frequency and a typical thick sample are shown in Fig.3 and Fig.4, respectively. The scattering angle range used here was 10°~60°. From Fig.3 three narrow peaks corresponding to the (111), (220) and (311) lattice plane Bragg reflections can be seen. The shoulder on the left side of the (111) Bragg reflection is due to the amorphous glass substrate, which gives rise to a broad band centered about 25°. XRD experiments with the range as wide as 10° to 120° have also been done, but no other peaks have ever appeared, in other words, there are three preferential crystalline orientations (111), (220) and (311) in the μc-Si:H thin films deposited with VHF plasma. Goerlitzer *et al*. have ever reported a strong preferential crystalline orientation at (220)[11]. However, in our deposition system, the similar result has never been observed except using the RF glow discharge. The average crystalline grain size of every crystalline orientation can be evaluated according to Debye-Schurr formula, but the data presented in Fig.3 may introduce big error because of the weak XRD signal due to the "thin" ($<1\mu$m) thickness of samples. In order to estimate the average grain size more accurately, XRD experiments on "thick" samples ($>10\mu$m) are made intentionally.

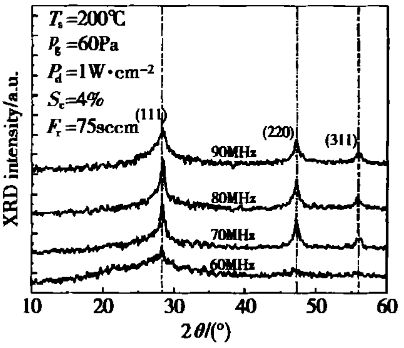

Fig.3 XRD signal with different plasma excitation frequencies

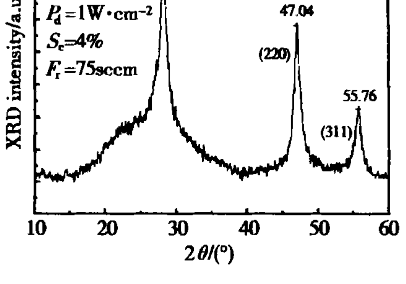

Fig.4 Typical XRD signal of a "thick" sample

Figure 4 is one of the typical results, from which we can estimate the different average grain sizes 8.5nm at (111), 9.6nm at (220) and 11.2nm at (311). The results are a little difference from that evaluated by Raman spectra. This difference can be explained with two possible reasons. First, both the evaluations with Raman and XRD are not very accurate to describe the real grain size in samples. Secondly there are some other crystalline orientation grains with very small size in the films that influence the Raman spectra but not observed in the XRD measurements. Certainly, this explanation needs to be further identified.

TEM and SAED are also used to characterize the micro-structural properties of μc-Si:H thin films. Samples used here were deposited on special copper nets. Figure 5(a) and (b) show the TEM dark-field image and the SAED pattern of a sample deposited at an condition described on the bottom of the figures, respectively. The result of TEM dark-field image is inferior to the SAED pattern for characterizing the crystallization of μc-Si:H films. The same preferential crystalline orientations as shown in the XRD experiments are clearly verified by SAED.

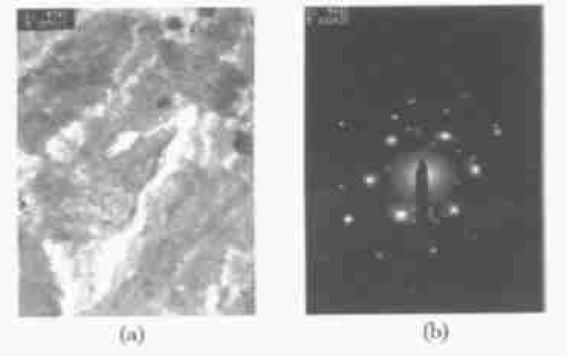

Fig.5 TEM dark-field image (a) and selected-area electron diffraction pattern (b) of sample deposited at 200℃, 80MHz, 60Pa, 75sccm, 1W/cm^2

4 Conclusions

In summary, we have succeeded in fabricating the μc-Si:H films at low temperature by VHF-PECVD technique. The investigations on series of films showed that VHF plasma can effectively lower the formation temperature of μc-Si:H film and enhance its deposition rate. Other deposition parameters such as T_s, p_g and P_d also strongly influence the deposition rate. Whereas, with the increase of the plasma power density, the deposition rate increased to a maximum at first, then decreased. The transitions from amorphous phase to the microcrystalline phase have been observed with varying the substrate temperature T_s and also with different silane concentration S_c, i.e. the crystallinity and the average grain sizes of μc-Si:H films strongly depended on T_s and S_c. The crystallinity is sensitive to plasma excitation frequency but the average grain size is not. Finally, three preferential crystalline orientations, corresponding to (111), (220) and (311) lattice planes, are obviously observed, and the average grain sizes are different for every crystalline orientation.

Acknowledgements The authors would like to thank F. Finger from ISI-PV Julich, Germany, for his valuable discussion on the deposition of μc-Si:H films, also to thank Dr. Wang Jiyou from North Jiaotong University and Dr. Xu Xiaoxuan from Nankai University for their help in the Raman scattering measurements.

References

[1] Meier J, Fluckigeret R, Keppner H, et al. Complete microcrystalline p-i-n solar cell-crystalline or amorphous cell behavior. Appl Phys Lett, 1994, 65(7): 860

[2] Shah A, Torres P, Tscharner R, et al. Photovoltaic technolology: the case for thin-film solar cells. Science, 1999, 285: 692

[3] Vetter O, Finger F, Carius R, et al. Intrinsic microcrystalline silicon: a new material for photovoltaics. Solar Energy Materials & Solar Cells, 2000, 62: 97

[4] Wehrspohn R B, Powell M J, Deane S C, et al. Dangling-bond defect state creation in microcrystalline silicon thin film transistors. Appl Phys Lett, 2000, 77(5): 1

[5] Stiebig H, Knipp D, Hapke P, et al. Three color piiin-detector using microcrystalline silicon. J Non-Cryst Solids, 1998, 227~230: 1330

[6] Matsumura H. Study on catalytic chemical vapor deposition

method to prepare hydrogenated amorphous silicon. J Appl Phys, 1989, 65(11): 4396

[7] Nozawa R, Takeda T, Ito M, et al. Substrate bias effects on low temperature polycrystalline silicon formation using electron cyclotron resonance SiH_4/H_2 plasma. J Appl Phys, 1997, 81(12): 8035

[8] Prasad K, Finger F, Dubail S, et al. Deposition of phosphorus doped microcrystalline silicon below 170℃ at 70MHz. J Non-Cryst Solids, 1991, 137～138: 681

[9] Luysberg M, Hapke P, Carius R, et al. Structure and growth of hydrogenated microcrystalline silicon: investigation by transmission electron microscopy and Raman spectroscopy of films grown at different plasma excitation frequencies. Phil Mag A, 1997, 75(1): 31

[10] Finger F, Müller J, Malten C, et al. Electronic states in hydrogenated microcrystalline silicon. Phil Mag B, 1998, 77(3): 805

[11] Goerlitzer M, Torres P, Beck N, et al. Structural properties and electronic transport in intrinsic microcrystalline silicon deposited by VHF-GD technique. J Non-Cryst Solids, 1998, 227～230: 996

[12] Shah A, Vallat-Sauvain E, Torres P, et al. Intrinsic microcrystalline silicon (μc-Si:H) deposited by VHF-GD (very high frequency-glow discharge): a new material for photovoltaics and optoelectronics. Mat Sci & Eng, 2000, B69～70: 219

[13] Peng Yingcai, Liu Ming, He Yuliang, et al. Conductive properties on doping nanometer silicon thin films. Chinese Journal of Semiconductors, 2000, 21(3): 308(in Chinese) [彭英才, 刘明, 何宇亮, 等. 掺杂 nc-Si:H 膜的电导特性. 半导体学报, 2000, 21(3): 308]

[14] Xu Ming, Wang Hongtao, Feng Lianghuan, et al. Periodic structure and quantum size effect of μc-Si:H/a-Si:H multilayers. Chinese Journal of Semiconductors, 2001, 22(4): 435 (in Chinese) [徐明, 王洪涛, 冯良桓, 等. μc-Si:H/a-Si:H 多层膜的周期性结构和量子尺寸效应. 半导体学报, 2001, 22(4): 435]

[15] Finger F, Kroll U, Viret V, et al. Influences of high exitation frequency (70MHz) in the glow discharge technique on the process plasma and the properties of hydrogenated amorphous silicon. J Appl Phys, 1992, 71(11): 5665

[16] Guo L, Kondo M, Fukawa M, et al. High rate deposition of microcrystalline silicon using conventional plasma-enhanced chemical vapor deposition. Jpn J Appl Phys, 1998, 37: L1116

[17] Fukawa M, Suzuki S, Guo L, et al. High rate growth of microcrystalline silicon using a high-pressure depletion method with VHF plasma. Solar Energy Materials & Solar Cells, 2001, 66: 217

[18] Kondo M, Matsuda A. Low temperature growth of microcrystalline silicon and its application to solar cells. Thin Solid Films, 2001, 383: 1

VHF-PECVD 法氢化微晶硅薄膜的低温制备*

杨恢东[1,2] 吴春亚[1] 麦耀华[1] 李洪波[1] 薛俊明[1] 李 岩[1]
任慧智[1] 张丽珠[3] 耿新华[1] 熊绍珍[1]

(1 南开大学光电研究所，天津 300071)
(2 五邑大学薄膜与纳米材料研究所，江门，529020)
(3 天津机电工业学校，天津 300071)

摘要: 采用 VHF-PECVD 方法，以高氢稀释的硅烷为反应气体，低温条件下成功地制备了系列 μc-Si∶H 薄膜. 对薄膜的厚度测量表明:增大激发频率和反应气压能有效提高沉积速率;随着等离子体功率密度的增大，沉积速率呈现出先增后减的变化. 薄膜的 Raman 光谱、XRD 及 TEM 等测试结果表明:提高衬底温度或减小硅烷浓度，可增大薄膜的结晶度和平均晶粒尺寸;等离子体激发频率的增大只影响薄膜的结晶度，并使结晶度出现极大值;薄膜中存在(111)、(220)和(311)三个择优结晶取向，且各结晶取向的平均晶粒尺寸不同.

关键词: 微晶硅薄膜；甚高频等离子体增强化学气相沉积；沉积速率；结晶度

PACC: 7360F；7280N；8115H

中图分类号: TN304.055 **文献标识码:** A **文章编号:** 0253-4177(2002)09-0902-07

---

* 国家重点基础研究发展规划资助项目(项目号:G20000282-2,G20000282-3)

杨恢东 男，1967 年出生，副教授，博士研究生，主要从事半导体薄膜材料与器件研究.

吴春亚 女，1969 年出生，副教授，主要从事光电材料与器件领域的理论研究.

熊绍珍 女，1939 年出生，教授，博士生导师，主要从事半导体器件与光电技术研究.

2002-01-18 收到，2002-04-08 定稿