Vol 14 No 11, November 2005
1009-1963/2005/14(11)/2348-04

Chinese Physics

© 2005 Chin. Phys. Soc.
and IOP Publishing Ltd

Study on stability of hydrogenated amorphous silicon films*

Zhu Xiu-Hong(朱秀红)[a], Chen Guang-Hua(陈光华)[a]†, Zhang Wen-Li(张文理)[a], Ding Yi(丁 毅)[b], Ma Zhan-Jie(马占洁)[a], Hu Yue-Hui(胡跃辉)[a], He Bin(何 斌)[a], and Rong Yan-Dong(荣延栋)[a]

[a] *Department of Materials Science and Engineering, Beijing University of Technology, Beijing 100022, China*

[b] *Department of Physics, Lanzhou University, Lanzhou 730000, China*

(Received 24 January 2005; revised manuscript received 20 June 2005)

Hydrogenated amorphous silicon (a-Si:H) films with high and same order of magnitude photosensitivity ($\sim 10^5$) but different stability were prepared by using microwave electron cyclotron resonance chemical vapour deposition system under the different deposition conditions. It was proposed that there was no direct correlation between the photosensitivity and the hydrogen content (C_H) as well as H–Si bonding configurations, but for the stability, they were the critical factors. The experimental results indicated that higher substrate temperature, hydrogen dilution ratio and lower deposition rate played an important role in improving the microstructure of a-Si:H films. We used hydrogen elimination model to explain our experimental results.

Keywords: hydrogenated amorphous silicon (a-Si:H) films, photosensitivity, stability, microstructure, hydrogen elimination (HE) model

PACC: 8115H, 6825, 6220

1. Introduction

It is necessary to understand the deposition mechanism of hydrogenated amorphous silicon (a-Si:H) in order to minimize its defect density and instabilities for applications such as solar cells and thin film transistors. Generally, it is considered that the deposition process consists of three stages, the creation of reactive species in a plasma, their reaction with the film surface and the conversion of surface layers into bulk a-Si:H, in which incorporated H atoms and H–Si bonding structures play a dominant role in determining the optoelectronic properties of a-Si:H films. It has often been reported that an increase in the Si-H_2 concentration causes a deterioration in photoconductivity, increased defect density and poorer photostability.[1−7] So, in order to control the material quality, it is essential to control the H bonding configurations depending critically upon H_2-dilution ratio, substrate temperature and growth rate etc. Clearly, it would be useful to do an experiment where one can independently study the effects of these parameters on deposition process. In this paper, we report on such a study, where the decomposition of silane is done by a microwave electron cyclotron resonance chemical vapour deposition (MWECR-CVD) system assisted by hot wire.

2. Experiment

The system used in this study is schematically illustrated in Fig.1. There are two chambers, the plasma chamber and the deposition chamber. The pumping system consists of a rotary pump and a turbomolecular pump. The base pressure $\sim 10^{-3}$Pa was achieved by the turbomolecular pump before each deposition. The microwave power is introduced into the plasma chamber through a rectangular waveguide and a ceramic window. The magnetic coil is arranged around the periphery of the plasma chamber and the magnetic field is applied to it for ECR plasma formation. The ECR condition is held at a magnetic flux density 875G. Power for sustaining the plasma is sup-

*Project supported by the National Basic Research Program of China (Grant No G2000028201-1).

†Corresponding author. E-mail: ghchen@bjut.edu.cn

plied from a microwave generator, which is modulated by a pulse generator. In addition, a hot wire system located 70mm above the sample holder to ensure the minimal radiative heat for the substrate is applied to supply thermal and ray radiations.

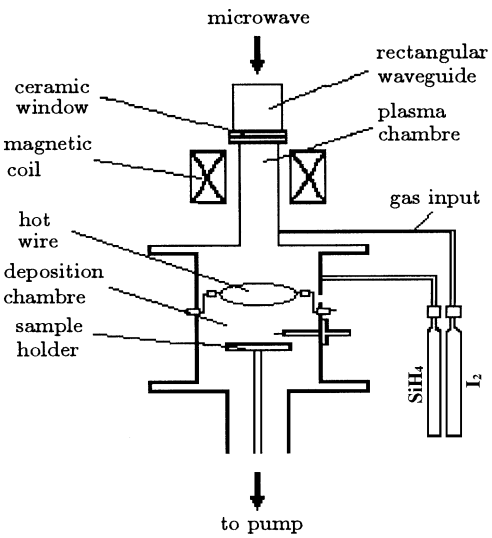


Fig.1. Schematic diagram of the MWECR-CVD apparatus.

Substrates used in the experiment are sheets of Corning 7059 glass for the measurements of thickness, optical gap and conductance of the films, and highly resistive crystalline silicon wafers are for the estimation of bonded hydrogen. The thickness of the films is measured by using a step apparatus and the deposition rate is obtained by the quotient of the thickness and deposition time. The photo- and dark conductivity are measured by Keithley 6517 Electrometer/High Resistance System.

The H–Si bonding configurations in as-deposited films are deduced from Fourier infrared transmission spectroscopy. The absorption band near 640cm^{-1} is assigned to the wagging mode of SiH_n (n=1, 2) and is proportional to the total hydrogen concentration. The stretching mode absorption is decomposed of two Gaussian curves centred at frequencies of ~2000 and ~2090cm^{-1}, corresponding to monohydride Si–H bonds and dihydride Si–H_2 or clustered void structures[8] respectively. And the integrated intensity ratio of 2000cm^{-1} and 2090cm^{-1} is defined as structure factor F, i.e. $F = I_{2000}/I_{2090}$.

3. Results

Table 1 lists the deposition condition of the a-Si:H films in the experiment. Here, we analyse two sets of samples. They are named as sample 1# and sample 2#, respectively, in which the former is deposited at lower substrate temperature and H_2-dilution ratio with higher deposition rate; the latter is deposited at higher substrate temperature and H_2-dilution ratio with lower deposition rate. The FITS spectra corresponding to two samples are shown in Fig.2. From the peak of 640cm^{-1} we can see that for the sample 2#, the total H content decreases in comparison with that of the sample 1#. As far as the stretching mode is concerned, it is not very clear to analyse the H–Si bonding configurations from Fig.2, so we turn to Gaussian fit to analyse, as shown in Fig.3. Obviously, we can see that in the sample 2#, there is much less polyhydride and dihydride bonds existed than that in the sample 1#, which are beneficial to decrease the defect density of a-Si:H films. Meanwhile, by calculation we also learn that $F_{\text{sample1\#}}$=1.35 and $F_{\text{sample2\#}}$=2.28, i.e. the structure factor of sample 2# is approximately two times bigger than that of sample 1#, which is consistent with our above results.

Table 1. Deposition conditions of a-Si:H films.

Background pressure/Pa	1.5×10^{-3}
H_2-dilution ratio	4:1, 7:1
Deposition pressure/Pa	2
Substrate temperature/°C	120, 200
Microwave power/W	500
Deposition rate/nm·s^{-1}	0.3, 1.5
Flux rate of SiH_4/sccm	20

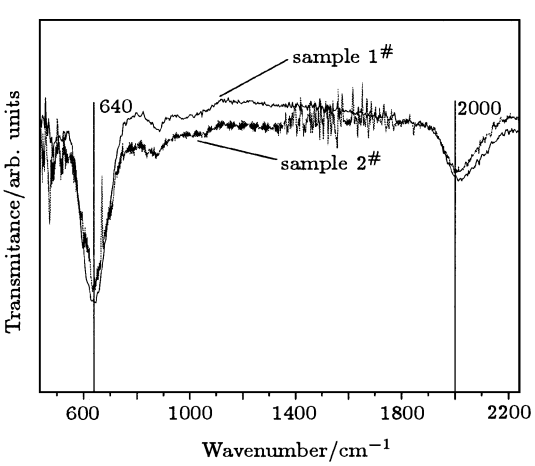


Fig.2. FTIR spectra of a-Si:H films growing under different deposition conditions.

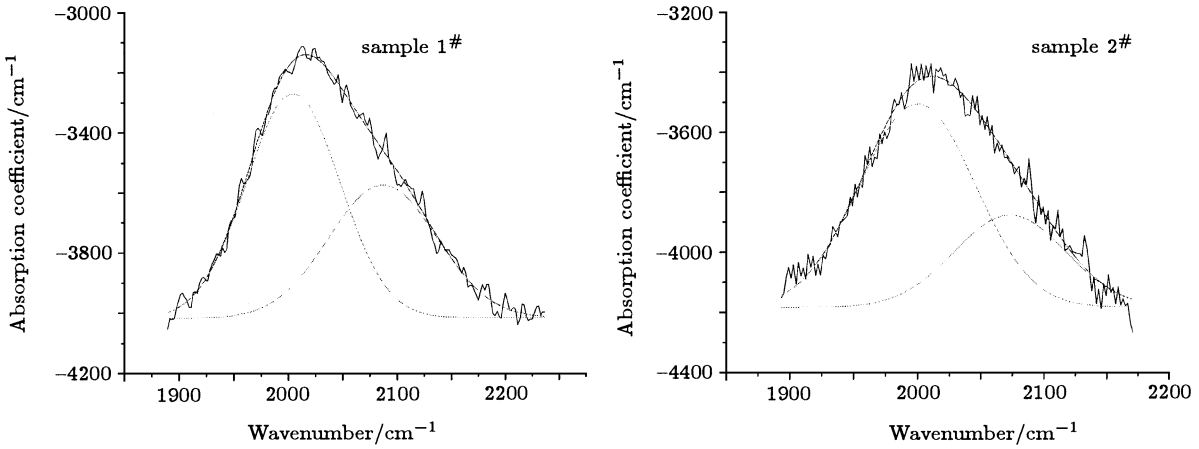


Fig.3. Gaussian fit curves for stretching mode.

In Fig.4, we showed the photodegradation curves, from which we can see clearly that with the prolongation of soaking time, the photoconductivity of the sample $2^{\#}$ trends to decrease slowly in comparison with that of the sample $1^{\#}$, although their photosensitivity is in the same order of magnitude.

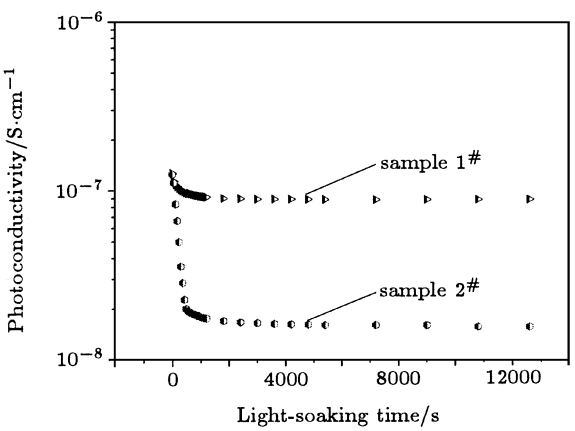


Fig.4. Dependence of the photoconductivity on light-soaking time in a-Si:H films.

4. Discussion

From the above results we can see clearly that the main factors determined the photostability are the hydrogen content and H–Si bonding configurations. According to the hydrogen elimination (HE) model,[9] the formation kinetics of H–Si bonding configurations during film growth is based on the thermally activated elimination of H atoms from SiH_3 precursors. So C_H is mainly determined by substrate temperature, which can be expressed as follows:[9]

$$T = 1000/\exp\{(C_H + b)/a\},$$

where a and b are constants. Obviously, we can see that the higher the temperature is, the lower the C_H is.

In the case of the high H_2-dilution process, because the activation energy of HE from monohydride is smaller than that from dihydride, based on the assumption of H abstraction reactions mediated through H_2-molecular formation,[10] abundant H^* radicals supplied from the plasma might reduce the activation energies for HE from polyhydrides and hence enhance the HE reactions. In addition, the high H_2-dilution deposition processes are thought to supply enough energy to cause HE and insertion reactions by H radicals or ions impinging on the surface. These reactions cause an active reconstruction of amorphous network, and result in random H-bonding configurations, which give the largest entropy for the arrangement of H atoms. As a result, the microstructure of a-Si:H films can be improved effectively.

Furthermore, under low deposition rate, it is beneficial for the HE from surface and the avoidance of the eliminated H recombination with Si again in the growth zone.

5. Conclusions

In conclusion, although a-Si:H films with high photosensitivity can be obtained under the different deposition conditions by using MWECR-CVD system, only by severely controlling the C_H and H–Si bonding configurations, a-Si:H films not only with high photosensitivity but also with high photostability can be prepared, in which higher substrate temperature and H_2-dilution ratio, and lower deposition rate played an important role.

References

[1] Mahan A H, Raboisson P and Tsu R 1987 *Appl. Phys. Lett.* **50** 335

[2] Nakamura N, Takahama T, Isomura M, Nishikuni M, Yoshida K, Tsuda S, Nakano S, Ohnishi M and Kuwano Y 1989 *Jpn. J. Appl. Phys.* **28** 1762

[3] Hishikawa Y, Tsuda S, Wakisaka K and Kuwano Y 1993 *J. Appl. Phys.* **73** 4227

[4] Hishikawa Y, Nionmiya K, Maruyana E *et al* 1994 *Proceedings of the 1st World Conference on the Photovoltaic Energy Conversion* (Waikoloa America, Hawaii) p386

[5] Okamoto S, Hishikawa Y, Tsuge S *et al* 1994 *Jpn. J. Appl. Phys.* **33** 1773

[6] Terakawa A, Shima M, Sayama K *et al* 1995 *Jpn. J. Appl. Phys.* **34** 1741

[7] Okamoto S, Hishikawa Y and Tsuda S 1996 *Jpn. J. Appl. Phys.* **35** 26

[8] Beyer W and Wagner H 1983 *Solid State Commun.* **48** 585

[9] Terakawa A 2002 *Phys. Rev.* B **62** 24

[10] Srinivasan E, Yang H and Parsons G N 1996 *J. Chem. Phys.* **105** 5467