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Preparation of hydrogenated microcrystalline silicon films with hot-wire-assisted MWECR-CVD system*

He Bin(何 斌)[a], Chen Guang-Hua(陈光华)[a]†, Zhu Xiu-Hong(朱秀红)[a], Zhang Wen-Li(张文理)[a], Ding Yi(丁 毅)[b], Ma Zhan-Jie(马占杰)[a], Gao Zhi-Hua(郜志华)[a], Song Xue-Mei(宋雪梅)[a], and Deng Jin-Xiang(邓金祥)[c]

[a] *College of Material Science and Engineering, Beijing University of Technology, Beijing 100022, China*
[b] *School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China*
[c] *College of Applied Science, Beijing University of Technology, Beijing 100022, China*

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Intrinsic hydrogenated microcrystalline silicon (μc-Si:H) films have been prepared by hot-wire-assisted microwave electron-cyclotron-resonance chemical vapour deposition (HW-MWECR-CVD) under different deposition conditions. Fourier-transform infrared spectra and Raman spectra were measured. Optical band gap was determined by Tauc plots, and experiments of photo-induced degradation were performed. It was observed that hydrogen dilution plays a more essential role than substrate temperature in microcrystalline transformation at low temperatures. Crystalline volume fraction and mean grain size in the films increase with the dilution ratio (R=H_2/(H_2+SiH_4)). With the rise of crystallinity in the films, the optical band gap tends to become narrower while the hydrogen content and photo-induced degradation decrease dramatically. The samples, were identified as μc-Si:H films, by calculating the optical band gap. It is considered that hydrogen dilution has an effect on reducing the crystallization activation energy of the material, which promotes the heterogeneous solid-state phase transition characterized by the Johnson–Mehl–Avrami (JMA) equation. The films with the needed structure can be prepared by balancing deposition and crystallization through controlling process parameters.

Keywords: HW-MWECR-CVD, μc-Si:H, hydrogen dilution, heterogeneous solid-state phase transition

PACC: 8115H, 7865P, 7830L, 6150K

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) has important applications in solar cells, large liquid crystal display, sensors and photoluminescence devices due to its unique properties and low-cost preparation processes. It has especially attracted considerable attention as material for absorber layers in solar cells.[1] The photovoltaic conversion efficiency of solar cell made of a-Si:H has reached 15.2% and stabilized efficiency of 13%.[2] Owing to the low carrier mobility and its inherent photo-induced degradation (Staeler–Wronski effect, SWE) in a-Si:H, however, the efficiency and further developments and applications are restricted. So, the study of a-Si:H concentrates on controlling SWE and improving the efficiency.

It is still difficult to explain all experimental facts presently by the several existing models[3–7] for SWE. The general opinion is that the new dangling bonds induced by light soaking are an essential element. These metastable defects cause the increase of capture coefficient and the decrease of mean carrier life, and then both photoconductivity and dark conductivity are reduced. In spite of difficulties in theory, the material which has weak SWE has been obtained in the processes based on preparation of a-Si:H, i.e. the hydrogenated microcrystalline silicon (μc-Si:H). The material, with microcrystalline phase embedded in an amorphous matrix, has received considerable attention for its high stability, improved carrier mobility and high doping efficiency as compared to a-Si:H, which ensure its bright prospect of application in thin film solar cells.[1,8,9] The highest efficiency of stacked solar cells composed of a-Si:H layers and μc-Si:H layers

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†E-mail: ghchen@bjut.edu.cn

is presently 14.7%.[2]

The common deposition process for μc-Si:H now is the plasma-enhanced chemical vapour deposition (PECVD).[10−13] Microwave electron-cyclotron-resonance chemical vapour deposition (MWECR-CVD), regarded as an important process because of its higher photon energy and easier to approach to excellent films, is a novel deposition technology developed in recent years.[14] Improvements has been made to the MWECR-CVD used in this study on the microwave coupling, the deposition rate and the properties of films deposited.[15] Especially, the hot wire was introduced to make the hot-wire-assisted MWECR-CVD (HW-MWECR-CVD). It has been found that this system could improve the microstructure and the optoelectronic properties of the a-Si:H films, and a trace of microcrystal occurred as well.[16] The schematic diagram of the system is illustrated in Fig.1. In this study, the μc-Si:H films are prepared by HW-MWECR-CVD and relevant measurements are performed. Discussion and analyses on the process and mechanism of microcrystal formation will be made depending on the results.

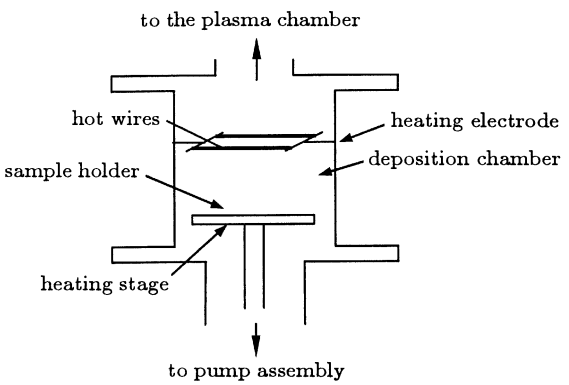


Fig.1. Schematic diagram of the HW-MWECR-CVD system used in this study.

2. Experimental procedure

Films were prepared under the conditions listed in Table1. Corning 7059 glass and (100) highly resistive crystal silicon were used as substrates. The former is for measuring thickness, optical band gap and photoconductivity of the films, and the latter for Fourier-transform infrared (FTIR) spectra and Raman scattering study. The hydrogen dilution (R=H_2/(H_2+SiH_4)) was controlled by gas flow meter and the substrate temperature (T_s) was controlled by CP11 high precision thermostat. Vacuum system consists of molecular pump and mechanical pump. Background pressure of 3.5×10^{-3}Pa was used. Two parallel tungsten filaments with a diameter of 0.5mm were used as hot wires, which were 50mm apart and 70mm above the sample holder. An AC transformer was employed to change the temperature of hot wires (T_{hw}) by changing the output voltage. The actual temperature was measured by infrared thermometer.

Table 1. Deposition conditions for preparation.

No.	T_s/°C	R/%	T_{hw}/°C	deposition pressure/Pa	microwave power/W
A	170	92	1300	2.0	450
B	170	95	1300	2.0	450
C	170	98	1300	2.0	450
D	170	92	room temperature	2.0	450
E	265	90	1300	2.0	450

FTIR spectra were measured by Xi'an-Chinetek FTIR 1020 Fourier spectrometer. Optical transmission and reflection data were obtained using SHIMADZU-3101PC UV-VIS-NIR scanning spectrophotometer, and the optical band gap of the films was determined by Tauc plot. The film thickness was measured by Surf Com 480A. Raman study was performed by Renishaw microscopic confocal Raman system (RM2000 spectrometer). SWE experiments were carried out by KEITHLEY 6517Electrometer/High Resistance System and simulated solar lamp with AM1 (100mW/cm^2) illumination.

3. Results and discussion

3.1. FTIR spectra

Infrared transmission spectroscopy is an important method for measuring the Si–H bond mode and calculating the hydrogen content. The characteristics and transformations of microstructure can be reflected in the spectrum. The shift of stretching mode peak from around 2000cm^{-1} to 2090cm^{-1} indicates

the rise of crystallinity.[17] As shown in Fig.2(a), it can be seen that hot wire is helpful and important for μc-Si:H preparation because of the obvious crystallinity in sample A prepared with hot wire. Figure 2(b) demonstrates the increase of crystallinity in the film with increasing R. It can be seen in Fig.2(c) that higher crystallinity occurs at higher R and lower T_s. It must be the higher R that makes higher crystallinity in sample A because higher substrate temperature will promote crystallization.[18] This shows the more essential and strong role the hydrogen dilution plays. In addition, the visible reduction of hydrogen content with rising crystallinity can be obtained from the wagging mode peaks around 640cm^{-1}. Relevant analysis will be given in section 3.5.

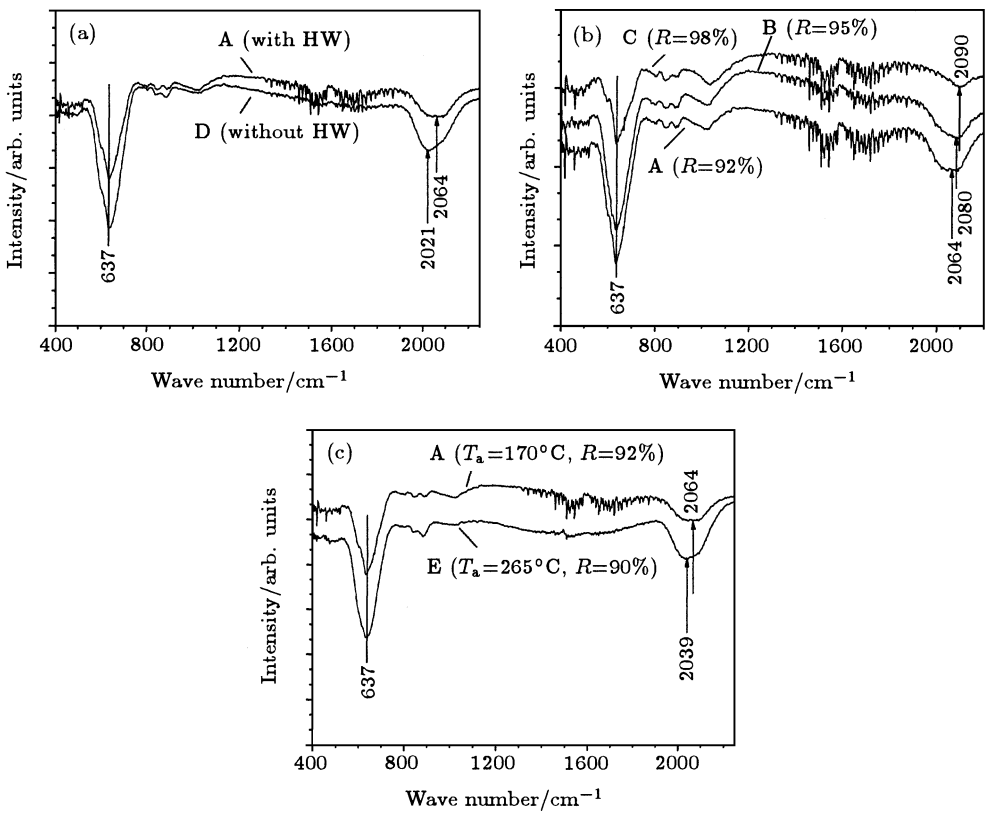


Fig.2. Comparisons between different FTIR spectra of samples. (a) Samples prepared at same R and T_s. (b) Samples prepared at different R and T_s=170°C. (c) Samples prepared at low T_s/high R and high T_s/low R.

3.2. Raman spectra

Raman spectra can be used to estimate the crystallinity further. Spectra of the samples prepared at different R and T_s=170°C are shown in Fig.3(a). The TO-like mode shifts gradually from 480cm^{-1} to crystalline silicon TO peak of 520cm^{-1}, together with increasing intensity, which implies the developing crystallinity and the transition to microcrystalline structure. Crystalline volume fraction (X_c) and mean size of the crystal grains (d) can be estimated by Gaussian fitting of Raman spectra. The TO-like mode peak was deconvolved into three parts: amorphous component peak at around 480cm^{-1}, crystalline component peak at around 520cm^{-1}, the scattering component peak at 495–509cm^{-1} corresponding to the expanding bond angles at grain boundaries.[19] X_c can be deduced from $X_c = (I_s + I_c)/(I_a + I_s + I_c)$,[20] where I_a, I_c and I_s denote the intensities of the amorphous, the crystalline and the boundary scattering components respectively. The Gaussian fitting result of sample B is shown in Fig.3(b) as an example, and the crystalline volume fraction is given by

$$X_c = (I_{497} + I_{511})/(I_{477} + I_{497} + I_{511}) = 20.4\%. \quad (1)$$

The values for samples A and C, 8.2% and 46.8% respectively, were obtained similarly. For the mean grain size we may calculate from the formula $d = 2\pi\,(B/\Delta\omega)^{1/2}$, where $\Delta\omega$ is the peak shift for the microcrystalline as compared with that of the c-Si,

and B=2.0 $cm^{-1}nm^2$.[21] The corresponding values for samples A, B and C, d=2.47nm, 2.95nm and 4.44nm respectively, can be easily obtained. So, both the crystallinity and the mean grain size rise in accordance with the dilution ratio.

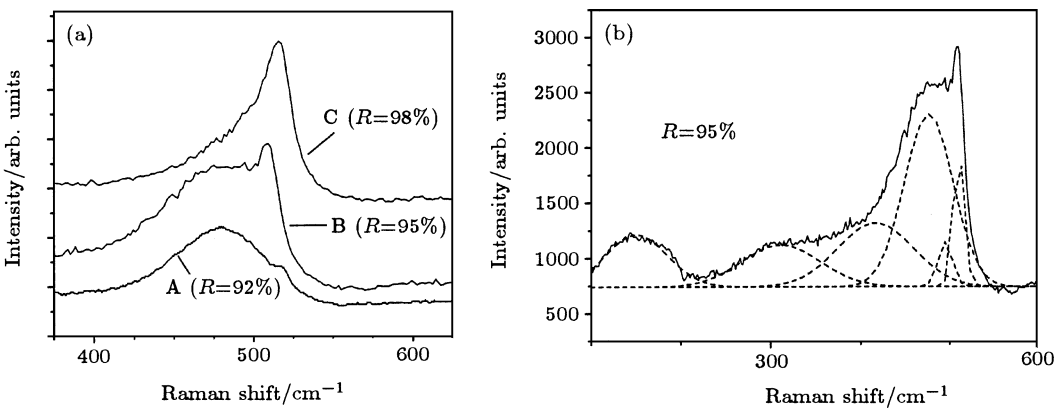


Fig.3. (a) TO-like mode in Raman scattering spectra of samples prepared at different R and T_s=170°C. (b) Raman scattering spectra and its Gaussian fitting of sample B.

3.3. Optical band gap tests

Figure 4 shows the Tauc plots of samples A, B and C. The deduced optical band gap of samples A, B and C are 1.72, 1.65 and 1.56eV respectively.

It is noted that the optical band gap decreases with increasing crystallinity. According to Ref.[22], optical band gap in a hydrogenated nano-amorph silicon (na-Si:H) film with grain size less than a certain value may be widened to 1.89eV due to the quantum confinement effect. With further increase of hydrogen dilution, there will be a transition from na-Si:H to μc-Si:H, in which the optical band gap decreases with increasing grain size. In Fig.4 the grain sizes in the samples have exceeded the nano-size range to produce quantum effects, which confirms the samples to be μc-Si:H films prepared in this paper. This comes obviously from strong hydrogen dilution.

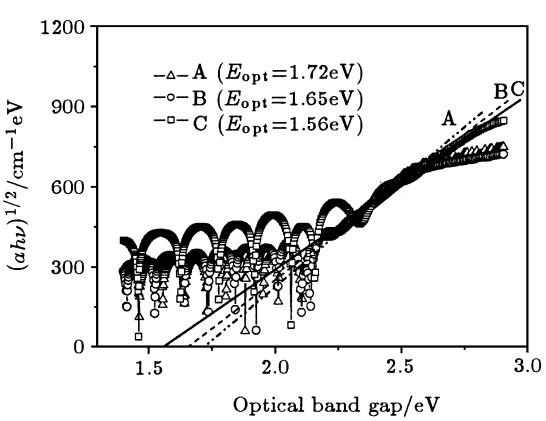


Fig.4. Tauc plots of samples prepared at different R and T_s=170°C.

3.4. SWE experiments

Photoconductivity was measured after Al electrodes were deposited to obtain SWE data. The degradation curves of photoconductivity of samples A, B and C are shown in Fig.5. It can be seen that the degradation decreases remarkably with increasing crystallinity. The strange light strengthening tendency even occurs in sample C, which is certainly due to microcrystalline phase formation. According to the results, SWE in μc-Si:H has been indeed restricted, which can help to improve the stability of devices.

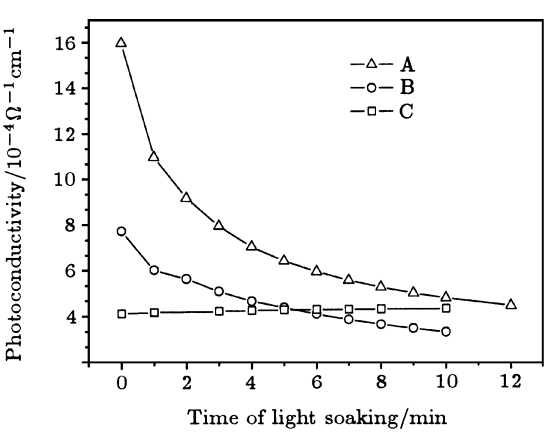


Fig.5. Dependence of the photoconductivity on light-soaking time of samples prepared at different R and T_s=170°C.

3.5. Mechanism analysis of microcrystal formation

At present, a general consensus for the mechanism of microcrystal formation in μc-Si:H has not been achieved yet. It is considered here that the formation of microcrystal during deposition is due to a chemical reaction process and a heterogeneous solid-state phase transition. Amorphous phase which has a natural crystallization tendency is the metastable state in thermodynamics. The formation of amorphous phase needs a considerable cooling rate, and it can only be prepared by vapour deposition in films for Si-based semiconductor materials.[23] Generally, amorphous materials have stability in kinetics for a certain potential barrier existing in amorphous structure in spite of instability in thermodynamics. An energy necessary for crystallization should be given, for instance, transformation from a-Si:H to polycrystalline silicon under high-temperature annealing through a heterogeneous solid-state phase transition. For similar reasons, higher substrate temperature will promote crystallization.[18] Whereas the substrate temperature in this study is much lower than crystallization temperature,[24] the crystallization in such low temperature process must be different from simple solid-state transition in high temperature annealing.

Attention should be paid to hydrogen dilution which is considered here the main factor for preparing μc-Si:H in low-temperature process of HW-MWECR-CVD since the above FTIR spectra have indicated that hydrogen dilution plays a crucial role. On the growth surface, as is well known, hydrogen atoms can break the weak Si–Si bonds and capture the H in Si–H bonds during deposition. This etching process will help to form firmer covalent bonds and tends to form a short-range-ordered structure. Then the nucleation and growth in the film will be enhanced by hydrogen dilution and the solid-state phase transition as well. The hydrogen content in the film will be reduced at the same time, which is consistent with FTIR results above. It is hydrogen dilution that arouses the crystallization, i.e. heterogeneous solid-state phase transition, at low temperatures.

The heterogeneous solid-state phase transition during deposition can be considered approximately as an isothermal transformation for the little fluctuation of substrate temperature, thus the relationship between crystalline volume fraction and time can be expressed in the Johnson–Mehl–Avrami (JMA) equation:[25]

$$W = 1 - \exp(-Kt^n), \tag{2}$$

where W is the crystalline volume fraction, t is transformation duration, K is kinetic velocity parameter. $K = k_0 \exp(-G_a/RT)$, where G_a is the activation energy for crystallization. As discussed above, hydrogen dilution can promote the nucleation and growth, in other words, G_a is lowered. Then, as seen in the results above, crystalline volume fraction will increase according to the JMA equation. Crystal nucleus cannot develop fully, however, because of limited time of reaction and deposition. The μc-Si:H structure consisting of microcrystalline phase and amorphous phase comes into being finally. The films with needed structure and properties can be prepared by balancing deposition and crystallization through controlling process parameters.

4. Conclusions

Intrinsic μc-Si:H films have been prepared by HW-MWECR-CVD. The investigation indicated that hydrogen dilution plays a more essential role than temperature for crystallization. Crystalline volume fraction and mean grain size in the films increases with the increase of hydrogen dilution ratio. With the rise of crystallinity in the films, the optical band gap has a decreasing trend, and the hydrogen content and photo-induced degradation reduce. It is considered that hydrogen dilution has an effect on reducing the crystallization activation energy of a-Si:H, which promotes the heterogeneous solid-state phase transition, and then the structure including both amorphous phase and microcrystalline phase can be gained. The films needed can be prepared by balancing the deposition and crystallization through controlling process parameters.

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