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Light induced microstructure transformation in a-Si:H films*

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A series of a-Si:H films are deposited by hot wire assisted microwave electron cyclotron resonant chemical vapour deposition (HW-MWECR-CVD), subsequently exposed under simulated illumination for three hours. This paper studies the microstructure change during illumination by Fourier Transformation Infrared (FTIR) spectra. There are two typical transformation tendencies of microstructure after illumination. It proposes a model of light induced structural change based on the experimental results. It is found that all samples follow the same mechanism during illumination, and intrinsic structure of samples affect the total H content.

Keywords: hydrogenated amorphous silicon, Staebler–Wronski effect, microwave electron cyclotron resonant chemical vapour deposition

PACC: 7000, 7155E, 7110

1. Introduction

The inevitable light induced degradation effect of a-Si:H films, i.e. the Staebler–Wronski effect (SWE),[1] seriously limits their further application in solar cells and electronic devices. Up to now, many researchers have done a lot of work to reveal the mechanism of light induced microstructure transformation and photoconductivity degradation.[2−5] It is generally accepted that light soaking results in large numbers of additional dangling-bond defects inside films. There are two typical models to describe the kinetics of light induced dangling-bond creation: weak-bond breaking due to carrier recombination and metastable dangling-bond creation by hydrogen collision. Both models lead to the same defect creation rate equation and the latter can be used to explain the dangling-bond creation at low temperature.[6,7] In this paper, we study the change of FTIR absorption spectra of a-Si:H films before and after light soaking and reveal the kinetics of light induced microstructure transformation.

2. Experiment

It is well known that plasma with higher density and lower temperature can be excited in microwave electron cyclotron resonant chemical vapour deposition (MWECR-CVD) system and plasma bombardment to the film-growing surface is weak. It is a very efficient film deposition technique. H content in a-Si:H films deposited with hot wire CVD system is lower and light-induced degradation is lighter than that of films deposited by other techniques. Therefore, we combined two potent deposition techniques together and developed a novel deposition system, hot wire assisted MWECR-CVD, which has been reported in other papers. Two parallel tungsten filaments locate above the sample holder with distance of 70 mm separated away from each other 50 mm. The length of the tungsten filament is 215 mm. An infrared temperature meter (Raytek Raynger 3i) was used to correlate the tungsten temperature with the tungsten voltage. In the experiment, we initialized the tungsten voltage as 9 V, corresponding to the temperature of 1120 °C.[8,9]

A series of samples were deposited by using this system with mixed silane (20% in H_2) as the reaction gas. The samples were deposited with different temperature, power, gas flux, reaction pres-

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sure, etc. FTIR spectra of films were measured by Xian-Chinetek FTIR 1020 Fourier spectrometers, subsequently, these samples were exposed under simulated light illumination (AM1 100 mW/cm^2) for three hours, and we measured the FTIR spectra after that.

3. Experimental results and discussion

FTIR absorption spectrum was obtained from the transmission spectrum with the BCC method.[10] In this transformation process, the refractive index of c-Si was taken to be 3.42. Furthermore, the real part of the refractive index of a-Si:H was taken constant over the measured range of 400–4000 cm^{-1}. The H content is calculated with wagging mode (640 cm^{-1}). The proportional constant between the hydrogen concentration and the integrated absorbance of the wagging mode was $A_{640} = 2.1 \times 10^{19}\,\mathrm{cm}^{-2}$. We investigate the film microstructure transformation by analysing the change of stretching mode (1850–2200 cm^{-1}) in FTIR spectrum.[11–13]

After illumination, stretching modes of all samples show the same transformation tendency. We just study two typical sample 1$^{\#}$ and 2$^{\#}$. Figure 1(a) shows the stretching mode of sample 1$^{\#}$ before three hours illumination. This absorption peak is fitted by using Gaussian double-peaks. Peak centres lie at 2017.1 cm^{-1} and 2101.6 cm^{-1} respectively. Peak areas are 17.779 cm^{-1} and 8.3642 cm^{-1} respectively; Fig.1(b) shows the stretching mode of sample 1$^{\#}$ after three hours illumination. Also, this peak is fitted by using Gaussian double-peaks. Peak centres lie at 2010.6 cm^{-1} and 2095.0 cm^{-1} respectively. Peak areas are 15.912 cm^{-1} and 10.452 cm^{-1} respectively. After three hours illumination, the peak area of lower absorption peak (LAP) which lies around 2000 cm^{-1}(A_{2000}) becomes small and the peak area of higher absorption peak (HAP) which lies around 2100 cm^{-1} (A_{2100}) becomes large. It was proposed that the LAP is associated with the Si–H stretch absorption and the HAP is associated with the polyhydrides (including clustered monhydrides SiH_x $x = 2$ or 3) vibration absorption and other clusters. Accordingly, A_{2000} is proportional to monohydrides Si–H content and A_{2100} are proportional to polyhydrides and clusters content.[14] Referring to this result, we suggest that Si–H bonds decrease and atomic clusters increase after illumination. In addition, peak centres of both the LAP and the HAP are redshifted after illumination. The H contents calculated from their wagging modes have no significant change before and after illumination, which are 4.71 at.% and 4.75 at.% respectively.

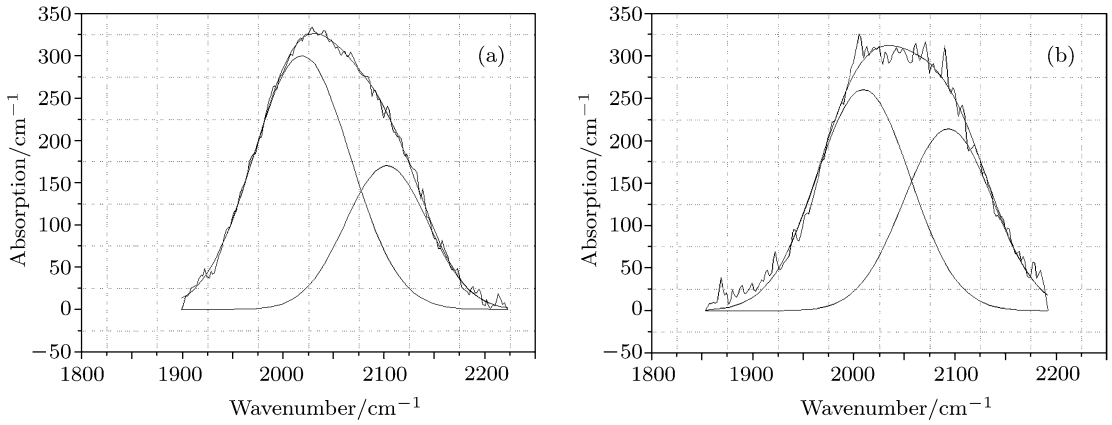


Fig.1. (a) The stretching mode of sample 1$^{\#}$ before three hours illumination, after fitting with Gaussian double-peaks, peak centres are 2017.1 cm^{-1} and 2101.6 cm^{-1} respectively, whereas peak areas are 17.779 cm^{-1} and 8.3642 cm^{-1} respectively. (b) The stretching mode of sample 1$^{\#}$ after three hours illumination, after fitting with Gaussian double-peaks, peak centres are 2010.6 cm^{-1} and 2095.0 cm^{-1} respectively, whereas peak areas are 15.912 cm^{-1} and 10.452 cm^{-1} respectively.

Figure 2(a) shows the stretching mode of sample $2^{\#}$ before three hours illumination. We fit this curve with Gaussian double-peaks. Peak centres lie at $2011.9\,\mathrm{cm}^{-1}$ and $2016.4\,\mathrm{cm}^{-1}$ respectively. Peak areas are $11.626\,\mathrm{cm}^{-1}$ and $2.2013\,\mathrm{cm}^{-1}$ respectively; Fig.2(b) shows the stretching mode of sample $2^{\#}$ after three hours illumination. After fitting with Gaussian double-peaks, peak centres lie at $2006.1\,\mathrm{cm}^{-1}$ and $2093.2\,\mathrm{cm}^{-1}$ respectively. Peak areas are $9.0311\,\mathrm{cm}^{-1}$ and $2.8262\,\mathrm{cm}^{-1}$ respectively. We note that the transformation tendency of stretching mode in sample $2^{\#}$ is similar to what we have observed in sample $1^{\#}$ after illumination. Nevertheless, the H content is reduced from 2.49at.% to 2.04at.% during the illumination, which is different from sample $1^{\#}$.

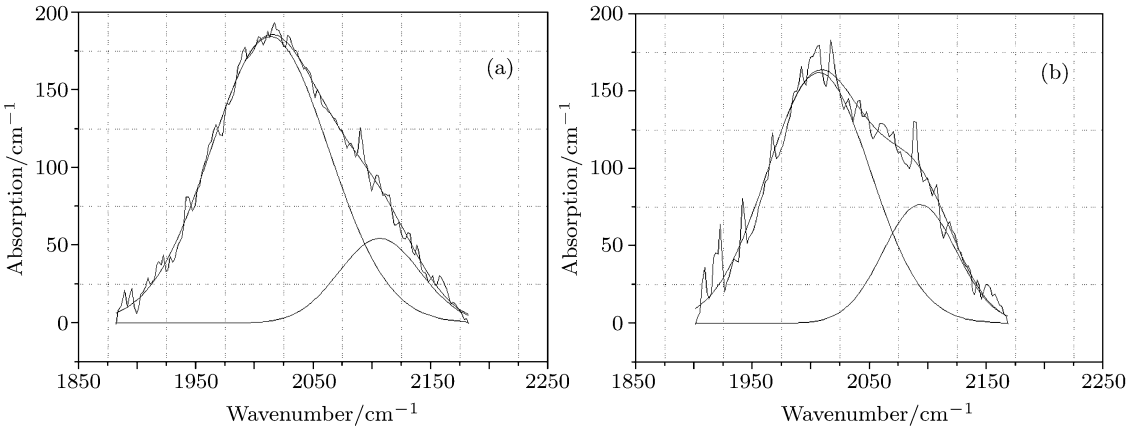


Fig.2. (a) The stretching mode of sample $2^{\#}$ before three hours illumination, after fitting with Gaussian double-peaks, peak centres are $2011.9\,\mathrm{cm}^{-1}$ and $2106.4\,\mathrm{cm}^{-1}$ respectively, whereas peak areas are $11.626\,\mathrm{cm}^{-1}$ and $2.2013\,\mathrm{cm}^{-1}$ respectively. (b) The stretching mode of sample $2^{\#}$ after three hours illumination, after fitting with Gaussian double-peaks, peak centres are $2006.1\,\mathrm{cm}^{-1}$ and $2093.2\,\mathrm{cm}^{-1}$ respectively, whereas peak areas are $9.0311\,\mathrm{cm}^{-1}$ and $2.8262\,\mathrm{cm}^{-1}$ respectively.

4. Discussion

The amounts of Si–H bonds decrease after the illumination. However, there needs about a relative high energy 3.6 eV for breaking Si–H bond.[15] Obviously, it is impossible to break Si–H bonds just by illumination. Actually, many researchers suggested that hydrogen from an isolated Si–H bond is inserted into a vicinity Si–Si bond, which form a Si–H–Si complex and a dangling-bond during illumination.[16,17] The possible mechanism is indicated as follows:

$$[\mathrm{Si}--\mathrm{H}]+[\mathrm{Si}--\mathrm{Si}]\rightarrow[\mathrm{Si}--]+[\mathrm{Si}--\mathrm{H}--\mathrm{Si}] \quad (1)$$

This reaction needs lower energy 1.74 eV. It can be easily initiated by recombination of tail state carriers, which results in a dramatic decrease of Si–H bond. And that is why A_{2000} is reduced after illumination. Si–H–Si complex is not stable because its H energy (about 1.0 eV) is low,[18] which has been proved by many other researchers. Many of them suggested that Si–H–Si complex is a transient state. In this case, we propose that by using assistance of heat or other types of energy, a possible reaction indicated in reaction (2) would be more likely:

$$2[\mathrm{Si}--\mathrm{H}--\mathrm{Si}]\rightarrow\ [\mathrm{Si}--\mathrm{H}--\mathrm{H}--\mathrm{Si}]+[\mathrm{Si}--\mathrm{Si}]\mathrm{weak}. \quad (2)$$

The H energies in Si–H–H–Si complex are 2.1 eV, which is higher than that of Si–H–Si[18] and this complex is more stable than Si–H–Si. The presence of Si–H–H–Si complex makes the absorption at $2100\,\mathrm{cm}^{-1}$ strong.

The total reaction which is a combination of reactions (1) and (2) is as follows:

$$2[\mathrm{Si}--\mathrm{H}]+2[\mathrm{Si}--\mathrm{Si}]\rightarrow\ [\mathrm{Si}--\mathrm{H}--\mathrm{H}--\mathrm{Si}]+[\mathrm{Si}--\mathrm{Si}]\mathrm{weak}+2[\mathrm{Si}--]. \quad (3)$$

The experimental data of sample $1^{\#}$ is in good agreement with the reaction (3). During illumination, many Si–H bonds are turned into Si–H–H–Si complex, which leads to the decrease of A_{2000} and the increase of A_{2100}. The presence of weak Si–Si bonds after illumination induces the microstructure relaxation in films,

which leads to the redshift of peak centre in both the LAP and the HAP.

However, the reaction (3) can not explain the phenomenon of reduction of H content which is observed in sample $2^{\#}$ after illumination. Actually, Si–H–Si complex created in reaction (1) favours the following reaction by the assistance of lower energy:

$$[\mathrm{Si}--\mathrm{H}] + [\mathrm{Si}--\mathrm{H}--\mathrm{Si}] \rightarrow [\mathrm{Si}-] + [\mathrm{Si}--\mathrm{Si}] + \mathrm{H}_2^{\mathrm{i}} \quad (4)$$

This reaction costs only about 0.2 eV. $\mathrm{H}_2^{\mathrm{i}}$ represents an interstitial hydrogen molecule. However, $\mathrm{H}_2^{\mathrm{i}}$ molecule is not sufficiently stable because it can be easily dissociated to two isolated H atoms by the assistance of lower energy, which could be derived from the nonradiation recombination of electrons or holes (or both). Once dissociated, the isolated H atoms would diffuse and passivate dangling-bonds in films, whereas $\mathrm{H}_2^{\mathrm{i}}$ molecule can be stored in microvoids of a-Si:H or platelets located close to the microcrystallites/a-Si:H interface when films are deposited on the edge of crystallization. It could not be thermally broken. Therefore, the reason of reduction of H content in sample $2^{\#}$ is that there are many voids or platelets in this film; hydrogen molecule created in reaction (4) is trapped into voids or platelets during illumination. Longeaud *et al* have also found that part of hydrogen molecules are trapped into the voids or platelets after illumination and these hydrogen molecules can not dissociate or passivate dangling-bands just by annealing. So the irreversible modifications of the deep defect density were observed.[15]

In fact, all samples have followed the same mechanism during illumination. Reactions (3) and (4) occur in all samples. However, there is little structure defection in the film if the microstructure of sample is compact. Analysing experimental result of sample $1^{\#}$, we find that $\mathrm{H}_2^{\mathrm{i}}$ created in reaction (4) would dissociate and become two H atoms immediately which can passivate the dangling-bonds. In this case, the reduction of H content can not be observed.

5. Conclusion

In order to reveal the micromechanism of light induced degradation in a-Si:H films, we study the microstructure transformation of samples during illumination by using FTIR spectra. There are two typical transformation tendencies of microstructure after illumination. We proposed our light induced microstructure transformation model and found that all samples follow the same mechanism during illumination, but the total H content changed in some samples because of their intrinsic structure.

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