Evolution of infrared spectra and optical emission spectra in hydrogenated silicon thin films prepared by VHF-PECVD*

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A series of hydrogenated silicon thin films with varying silane concentrations have been deposited by using very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) method. The deposition process and the silicon thin films are studied by using optical emission spectroscopy (OES) and Fourier transfer infrared (FTIR) spectroscopy, respectively. The results show that when the silane concentration changes from 10% to 1%, the peak frequency of the Si–H stretching mode shifts from 2000 cm^{-1} to 2100 cm^{-1}, while the peak frequency of the Si–H wagging–rocking mode shifts from 650 cm^{-1} to 620 cm^{-1}. At the same time the SiH^*/H_α intensity ratio in the plasma decreases gradually. The evolution of the infrared spectra and the optical emission spectra demonstrates a morphological phase transition from amorphous silicon (a-Si:H) to microcrystalline silicon (μc-Si:H). The structural evolution and the μc-Si:H formation have been analyzed based on the variation of H_α and SiH^* intensities in the plasma. The role of oxygen impurity during the plasma process and in the silicon films is also discussed in this study.

Keywords: Fourier transfer infrared spectroscopy, optical emission spectroscopy, Si–H bonding configuration, oxygen impurity

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1. Introduction

At present, the very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) method is attracting considerable attention for the high-rate deposition of highly stable a-Si:H and μc-Si:H thin-film solar cells.[1,2] During the deposition of silicon films and solar cells, the process parameters, such as hydrogen dilution, plasma power and deposition pressure, strongly influence the plasma particles, the plasma density and the ion energy distribution, which then determine the deposition process and the film properties.[3] Among these process parameters, hydrogen dilution has been widely used in the fabrication of highly efficiency and highly stable a-Si:H and μc-Si:H solar cells.[1−4]

In order to produce device-quality silicon films, the relationship between deposition parameters, plasma characteristics, micro-structural and opto-electronic properties should be studied. Many research works are related to film properties, while few of them correlate the plasma process with film properties. In this paper, the influence of hydrogen dilution on the plasma process and on the opto-electronic and structural properties of silicon films is investigated. In-situ optical emission spectroscopy (OES) and ex-situ Fourier transfer infrared (FTIR) spectroscopy are used to study the deposition process and the film properties. The oxygen impurities during the plasma process and in the silicon films are also studied.

2. Experimental details

The silicon thin films in this study were prepared by using the capacitively coupled PECVD technique with the excitation frequency of 60 MHz on 7059 glass substrates and double-side-polished c-Si wafers. The base pressure of the deposition system was below 2×10^{-4} Pa. The other deposition conditions included the plasma power of 15 W, a working pressure of 60 Pa and a substrate temperature of 200 °C. Silane mixed

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with hydrogen was used as the feed gas. The silane concentration (S_c=[SiH_4]/[SiH_4]+[H_2]) was changed from 1% to 10%.

The thicknesses of these samples were from 0.8 μm to 1.2 μm. The FTIR measurement was done with a 170XS (Nicolet, USA) at wavenumber range from 400 cm^{-1} to 4000 cm^{-1} and at a resolution of 0.06 cm^{-1}. Optical emission spectroscopy was recorded through a quartz window in the wavelength range from 380 nm to 780 nm to diagnose the SiH^* (412 nm) and the H_α (656 nm) emissions from the plasma. The Raman scattering measurement was carried out with the 632.8 nm line of a He–Ne laser.

3. Results and discussion

3.1. FTIR spectra of silicon films

FTIR spectroscopy is an effective method to study the hydrogen content and silicon-hydrogen bonding configurations of the hydrogenated silicon thin films. In addition, information about oxygen and carbon impurities can be obtained from the FTIR spectra.[5–7] Figure 1 shows the FTIR spectra of silicon films prepared at different silane concentrations. Four typical peaks appear in the FTIR spectra:[8,9]

1) the peak centered at 630 cm^{-1}–640 cm^{-1} due to the Si–H wagging–rocking modes;

2) the peak centered at 840 cm^{-1}–890 cm^{-1} due to the Si–H bending modes;

3) the peak centered at 2000 cm^{-1}–2100 cm^{-1} due to the Si–H stretching modes;

4) the peak centered at 1000 cm^{-1}–1200 cm^{-1} due to the Si–O stretching modes.[5–7]

The most interesting feature in the FTIR spectra is the evolution of the Si–H wagging–rocking and the Si–H stretching modes. It is obvious from Fig. 1 that when the S_c decreases, the peak frequency of the Si–H stretching mode shifts from 2000 cm^{-1} to 2100 cm^{-1}, and the peak frequency of the Si–H wagging–rocking mode shifts from 650 cm^{-1} to 620 cm^{-1}. In order to get more information about the Si–H bonding configurations, the wagging–rocking mode is fitted using two Gaussian functions centered at ∼650 cm^{-1} and ∼620 cm^{-1}, as shown in Fig. 2. The ∼650 cm^{-1} peak pertains to a bonding structure of a typical a-Si:H, and the ∼620 cm^{-1} peak is regarded as an indication of changes in the hydrogen bonding environment or of the appearance of microcrystalline grains embedded in the amorphous matrix.[9] The 620 cm^{-1} component appears in all FTIR spectra and the relative intensity, defined as $\Delta I_{620} = I_{620}/(I_{650}+I_{620})$,[9] increases with S_c decreasing, as shown in Fig. 4.

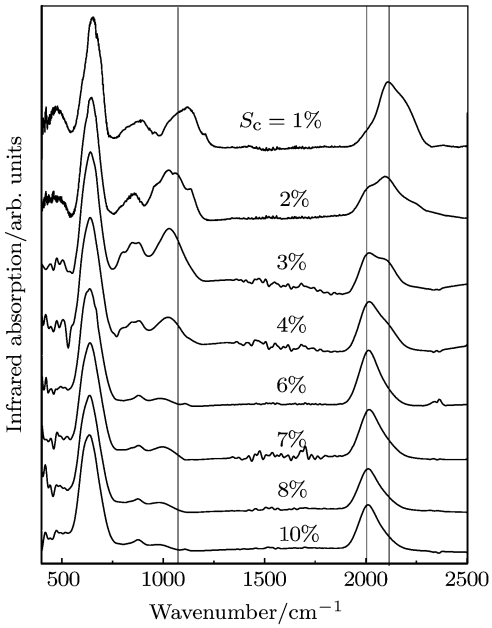


Fig. 1. FTIR spectra of silicon films prepared at different S_c's.

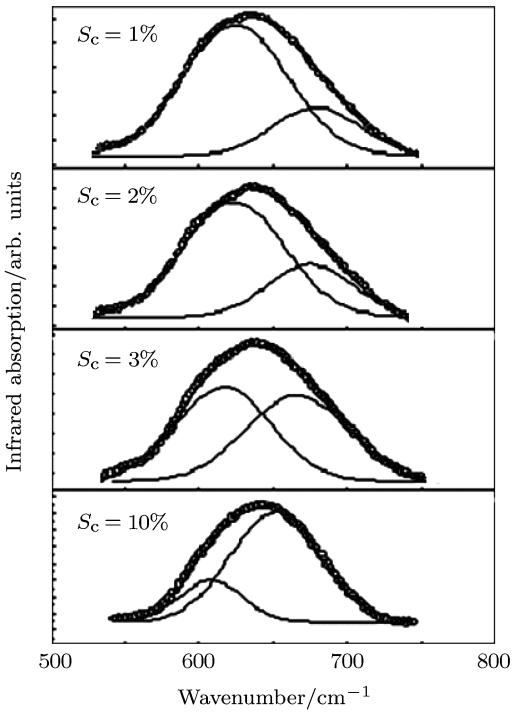


Fig. 2. De-convoluted wagging–rocking modes of silicon films prepared at different S_c's.

For films with S_c ranging from 3% to 10%, the Si–H stretching mode can be de-convoluted into two Gaussian functions centered at 2000 cm^{-1} and 2100 cm^{-1}. For films with S_c = 1% and 2%, three Gaussian functions are used and the third mode peaks

at ∼2180 cm^{-1}. The results are shown in Fig. 3. In typical a-Si films, the 2000 cm^{-1} component originates from the stretching vibration of the mono-hydride SiH, and the 2100 cm^{-1} component can be attributed to the clustered SiH bonds, including $(SiH)_n$, SiH_2, $(SiH_2)_n$ and so on.[9,10] The 2100 cm^{-1} peak appears in all FTIR spectra and the relative intensity, defined as $\Delta I_{2100} = I_{2100}/(I_{2000}+I_{2100})$, increases with S_c decreasing, as shown in Fig. 4. In a-Si:H films, ΔI_{2100} is also called the microstructural parameter, which is an indication of the appearance of H-clusters and Si–H bonds on the internal surfaces of the micro-voids.[10] When S_c varies from 10% to 6%, the microstructural parameters are around 0.2, which demonstrates the high quality of our a-Si:H films.[10] For $S_c \leq 4\%$, ΔI_{2100} becomes much higher. Does this demonstrate that more micro-voids exist in these films? Or is there another reason for the 2100 cm^{-1} vibration? When the samples are deposited with $S_c \leq 4\%$, it is suitable for the formation of the microcrystalline silicon, which is obvious from the Raman results in Fig. 5. Since ΔI_{2100} and ΔI_{620} evolve in a similar manner, they should have the same origination. In other words, the 2100 cm^{-1} peak is related with the microcrystalline structure. In fact, several groups have suggested that the higher ΔI_{2100} is related to the microcrystallinity in silicon films. Cardona believed that if no $(SiH_2)_n$ mode appeared in 840 cm^{-1}–890 cm^{-1}, the stretching mode at 2100 cm^{-1} should be associated with the SiH bonds on the surface of the silicon crystallites.[11] Kroll also supported this standpoint and regarded it as a sign of the occurrence of microcrystallinity.[10] Deng assigned the 2100 cm^{-1} modes to the H_2^* complexes in the boundaries between microcrystallites.[12] Therefore, there are different originations for the 2100 cm^{-1} vibrations in a-Si:H and μc-Si:H films. The 2100 cm^{-1} peak is related to the micro-voids and clustered SiH bonds in a-Si:H films, while it originates from the microcrystallinity in μc-Si:H films. Based on the evolution of ΔI_{620} and ΔI_{2100}, a morphological phase transition from a-Si:H to μc-Si:H occurs in the narrow region ($6\% < S_c < 4\%$) in this study. This phase transition is also demonstrated by the Raman results in Fig. 5.

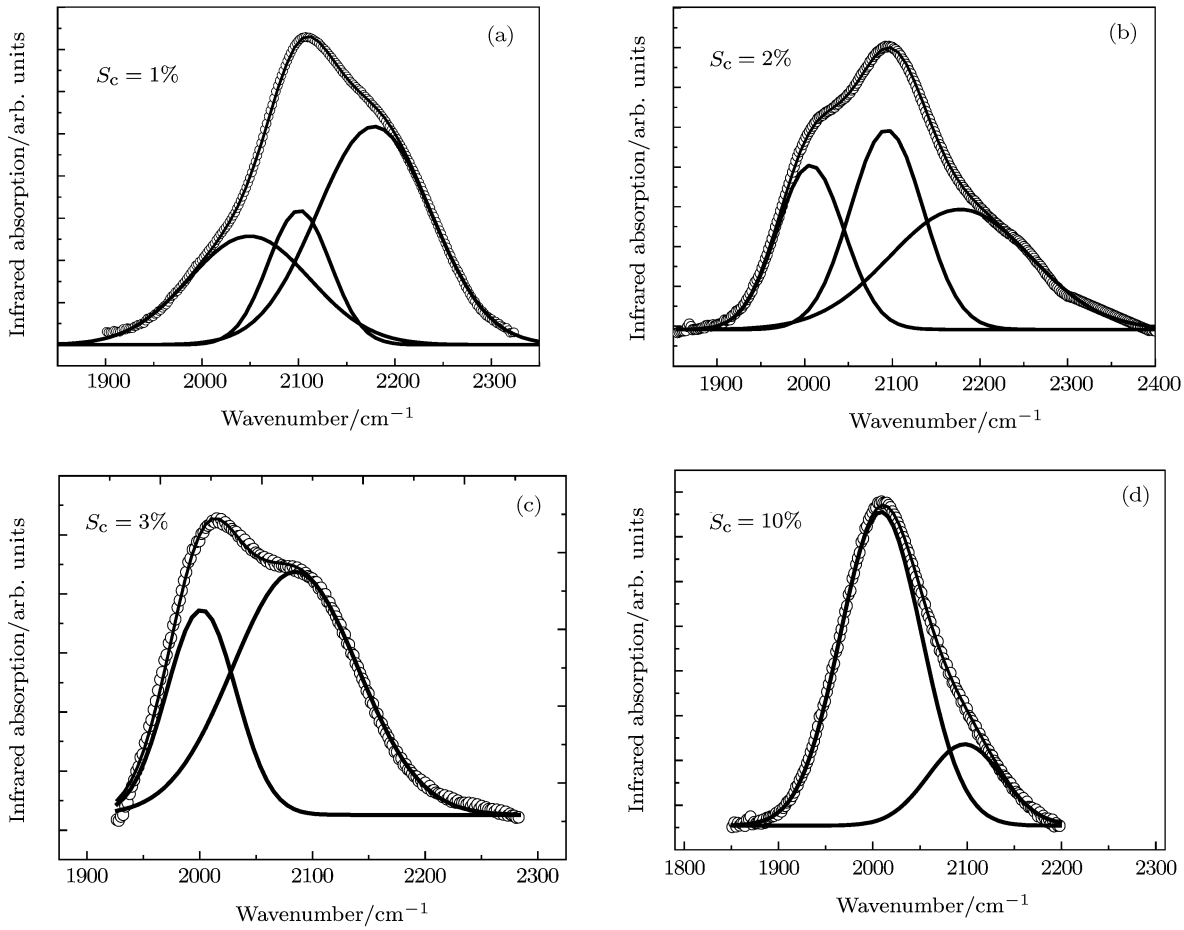


Fig. 3. De-convoluted Si–H stretching modes of silicon films prepared at different S_c's: (a) $S_c = 1\%$, (b) $S_c = 2\%$, (c) $S_c = 3\%$, and (d) $S_c = 10\%$,

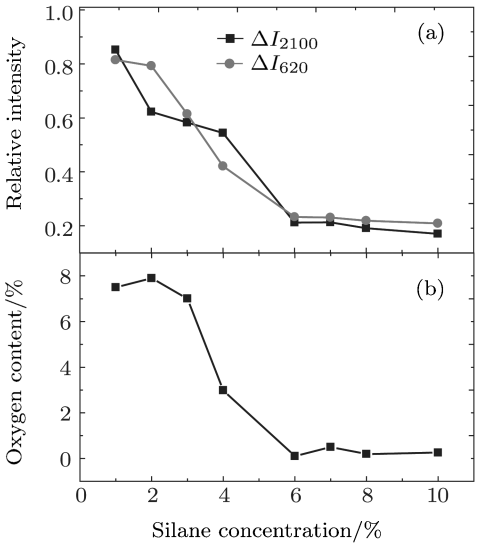


Fig. 4. The (a) ΔI_{620}, ΔI_{2100} and (b) oxygen content each as a function of S_c.

At a higher hydrogen dilution level (mainly with $S_c \leq 4\%$), above which the microcrystallinity starts to form, a Si–O absorption band at 1000 cm^{-1}–1200 cm^{-1} appears. The Si–O absorption intensity gradually increases and the peak absorption also shifts to a higher frequency. When S_c are 1% and 2%, the silicon films are highly crystallized, the Si–H stretching modes consist of not only typical 2000 cm^{-1} and 2100 cm^{-1} modes, but also an additional mode around 2180 cm^{-1}. All these features indicate enhanced oxygen incorporation in highly crystallized silicon films.[5–8] With the oxygen content increasing, some oxygen atoms are bonded to the silicon network. Due to the higher electronegativity of the oxygen compared to that of the silicon, a redistribution of the electric charge along with a change in the bonding energy of SiH_x is possible. Then the Si–O stretching mode as well as the Si–H stretching mode shifts to a higher frequency. Namita Dutta Gupta and Partha Chaudhuri have also observed this frequency shift and pointed out that is strongly depends on the number of the oxygen atoms back-bonded to the SiH or SiH_2 groups.[6] When S_c are 1% and 2%, the additional bond around 2180 cm^{-1} can be attributed to the SiH_2 bonded with two oxygen atoms. In previous studies, authors attributed the increased Si–O bond intensity to the fast oxidation in air resulting from the porous-like structure.[5,7] After our samples were stored in air for several months, the 640 cm^{-1} and 2000 cm^{-1} modes had negligable changes, while 1000 cm^{-1}–1200 cm^{-1} Si–O mode increased sharply. This can be attributed to post oxidation resulting from the porosity of the microcrystalline silicon.[5,7,8] Another contribution to the increased Si–O intensity comes from the oxygen impurity incorporated during the deposition process, which will be analyzed with and supported by the OES results in Section 3.3. When keeping the other deposition parameters at constants, a high hydrogen dilution leads to a decrease of the deposition rate, which then enhances the probability of oxygen doping in silicon films.[13,1] The films are microcrystalline silicon at high hydrogen dilution, and the complex microstructure of μc-Si:H leads to a higher doping efficiency of μc-Si:H compared to that of a-Si:H. As we all know, μc-Si:H is highly sensitive to the incorporation of unintentional impurities, such as carbon, nitrogen and oxygen.[14,15] As a result, the oxygen-related FTIR peaks are much more pronounced in the μc-Si:H films. The oxygen content, obtained by integrating the area under the SiO absorption peak, is plotted as a function of S_c in Fig. 4.

3.2. Raman spectra of silicon films

Since different phases (amorphous or crystalline phase) in silicon films will result in different scattering peaks, Raman scattering spectroscopy has been widely used to characterize the film structure.[4] The peak at 520 cm^{-1} can be attributed to the crystalline phase, while the 480 cm^{-1} peak is related to the amorphous phase.

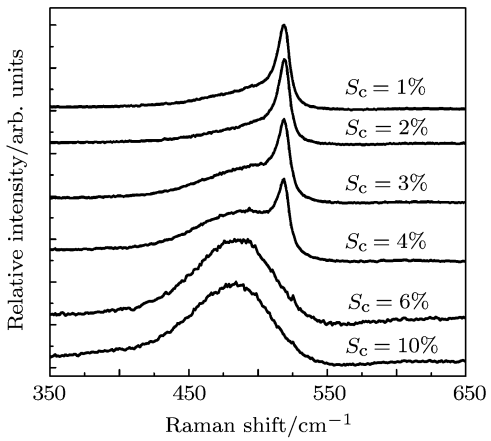


Fig. 5. Raman spectra of silicon films prepared at different S_c's.

Figure 5 shows Raman spectra of silicon films prepared at different S_c's. It can be seen that the silane concentration plays a very important role in the structural evolution. A phase transition from a-Si:H to μc-Si:H is also observed. When the S_c is higher than 6%, the films mainly show amorphous phase, characterized by a scattering broadband at $\sim$480 cm^{-1}. At S_c of 4%, besides an amorphous broadband at 480 cm^{-1}, a crystalline band peaked at 520 cm^{-1} also appears,

which indicates the presence of the μc-Si:H phase. Decreasing S_c further, the amorphous broadband disappears gradually, and the width of the crystalline band becomes narrower and narrower, which indicates enhanced crystallinity.

3.3. Optical emission spectra during the deposition of silicon films

Optical emission spectroscopy is a simple and efficient in-situ characterization technique, which does not disturb the plasma and has been successfully used for the diagnosis of the reactive plasma and for the control of the thin film deposition process.[16−23]

In this study, in order to get more information about the hydrogen diluted silane plasma, to understand the deposition process, and to investigate the evolution of the structural and the electronic properties, the OES was carried out to determine the change in the gas dissociation. Figure 6 shows the typical OES during the deposition of the silicon films. The interesting lines are H_α (656 nm) and SiH^* (412 nm), which have been reported to be good measures of the atomic hydrogen and the precursors SiH_x ($x = 1 - 3$).[16−23] The SiH^*, H_α intensities and the SiH^*/H_α intensity ratio as a function of S_c are plotted in Fig. 7. It can be seen that with S_c increasing, the SiH^* intensity increases gradually, while there is a slight decrease of H_α intensity. Thus the SiH^*/H_α intensity ratio increases from 0.86 ($S_c = 1\%$) to 3 ($S_c = 10\%$).

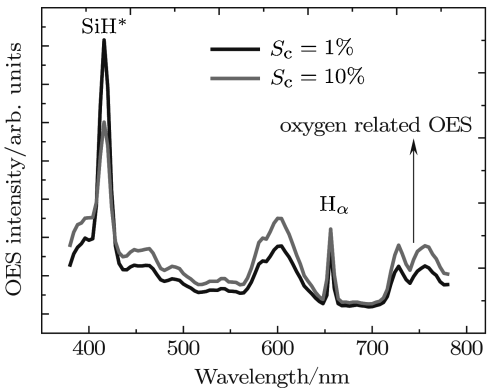


Fig. 6. Typical OES during deposition of silicon films prepared at S_c's of 1% and 10%.

It is well known that there are several reactions in the hydrogen diluted silane plasma:[23] (1) the production of the deposition precursors SiH_x ($x = 1$, 2, 3); (2) the production of the atomic hydrogen, which mainly results from the primary electron-silane reaction, $SiH_4 + e \rightarrow (4 - x)H + SiH_x$, and from the electron-hydrogen reaction, $H_2 + e \rightarrow H + H$; (3) the annihilation of the atomic hydrogen through the recombination reaction, $H + SiH_4 \rightarrow H_2 + SiH_3$. Although different models have been developed for the μc-Si:H formation,[24,25] they all agreed that sufficient atomic hydrogen is a necessary and crucial factor for the μc-Si growth.[21,23] In order to get μc-Si:H, the deposition conditions should be suitable for the production of the atomic hydrogen and for the inhibition of the annihilation reaction. When S_c is higher, many more silane molecules will annihilate the atomic hydrogen, which leads to a lower H_α emission intensity, as a result the SiH^*/H_α intensity ratio is higher. With S_c decreasing gradually, the high hydrogen dilution compensates for the annihilation reaction and allows for a higher atomic hydrogen flux than that of SiH_x, thus a more ordered network forms. As described in Refs. [17]–[20], the SiH^*/H_α intensity ratio is a decisive criterion to predict crystallinity. When this ratio becomes low enough, microcrystallinity starts to form. In our case, the SiH^*/H_α intensity ratios are 1.7 and 2.3 at S_c's of 4% and 6%, respectively. A morphological phase transition from a-Si:H to μc-Si:H takes place with S_c between 4% and 6%, which is consistent with the above FTIR and Raman spectra.

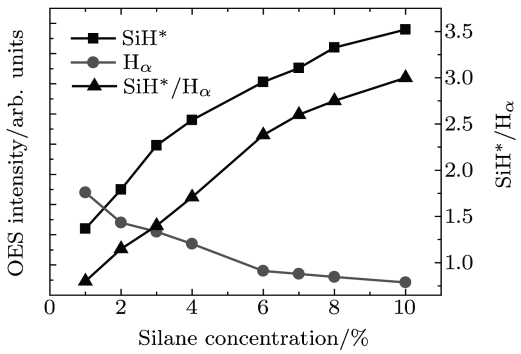


Fig. 7. OES intensities of SiH^* and H_α and SiH^*/H_α intensity ratio as a function of S_c.

Furthermore, the OES can also give information about the oxygen impurity during the plasma deposition. The spectrum range from 712 nm to 780 nm is regarded as the contributions from the oxygen-related transition $^5S^02 \rightarrow {}^5P3$.[22] This emission band appears in all OES (a-Si:H or μc-Si:H). When the S_c is higher, the film is a-Si:H, which has a lower doping efficiency. Although the oxygen-related emission is high in the OES, only a small part of the oxygen is bonded in the bulk film, which is then detected by the corresponding FTIR spectra. In addition, when the S_c is suitable for the μc-Si:H growth, the doping efficiency is higher. Many more oxygen atoms are bonded in

the bulk film and the corresponding oxygen-related peaks at ∼1050 cm^{-1} and 2180 cm^{-1} are present in the FTIR spectra.[5,6,19]

4. Conclusion

We have studied the influence of hydrogen dilution to the deposition process and to silicon film properties by using OES, FTIR and Raman spectra. Both results indicate a morphological phase evolution of the hydrogen-diluted silicon films from a-Si:H to μc-Si:H. From the OES results, we have confirmed that the variation of the SiH^* and the H_α emission intensities can be used to analyse the formation of the microcrystalline silicon. The oxygen impurity demonstrates different doping behaviours in a-Si:H and μc-Si:H films.

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