

Investigation of Cat-CVD amorphous silicon film properties under high catalyzer temperature

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In this study, we investigated the a-Si films which were deposited by Cat-CVD in the higher catalyzer temperature (T_{cat}) regime. We studied the influence of high T_{cat} on amorphous silicon (a-Si:H) thin-film properties. The information on a-Si-H bonding configuration was ob-

tained by Fourier Transform Infrared Spectroscopy (FTIR). The film defect density was investigated by the electron spin resonance (ESR) as a function of T_{cat} , the distance between catalyzer and substrate (D_{cs}), and the deposition pressure (P).

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1 Introduction Recently, silicon thin-film solar cells deposited by catalytic chemical vapor deposition (Cat-CVD) system have attracted much attention. Compared to the conventional plasma-enhanced CVD (PECVD), Cat-CVD seemed promising for depositing high quality amorphous-silicon [1, 2] or microcrystalline silicon thin films at higher deposition rate. It also showed the advantage of better silane usage during film deposition. However, the short lifetime of the tungsten filament, or the catalyzer, presents a severe limitation to this technology, which is due to the silicidation effect [3]. Increasing the catalyzer temperature may be an effective approach in prolonging the catalyzer lifetime [4]. However, this may raise the substrate temperature, causing serious degradation of the silicon film properties. In this study we focused on the high T_{cat} regime. The effects of " T_{cat} " on a-Si thin-film quality were investigated by changing deposition parameters such as the distance between catalyzer and substrate (D_{cs}), gas pressure and gas flow rates. We were able to find ways to obtain high quality a-Si thin-film even at high T_{cat} .

2 Experimental The a-Si:H thin-film samples were deposited at high T_{cat} ($>1900^{\circ}\text{C}$). Tungsten filament was used as the catalyzer here, which was found to be most efficient for silicon radical production [5]. In order to hold a

constant species flux (Si-related radicals) near the substrates, we increased the D_{cs} while the T_{cat} was raised. In addition, we raised the holder temperature from 400°C to 500°C to compensate for the reduction of thermal radiation when D_{cs} increased from 4 cm to 24 cm. The actual substrate temperature, estimated from the temperature-sensitive paint strips, was between 360°C and 410°C . In this study, the estimated catalyzer temperature (T_{cat}) was in the range of $1950\text{--}2050^{\circ}\text{C}$; the D_{cs} was varied between 4 to 24 cm; the P was varied between 1.1 Pa to 8 Pa; and the SiH_4 gas flow rate was varied between 50 to 200 sccm while the H_2 gas flow rate was also varied between 10 to 40 sccm. The deposition rate of a-Si thin-film attained was in the range of 26–140 nm/min. The defect density was estimated from the measurement of electron spin resonance (ESR). The information on Si-H bonding configuration was obtained by Fourier Transform Infrared Spectroscopy (FTIR), in which peaks near 2000 cm^{-1} and 2090 cm^{-1} correspond to Si-H and Si= H_2 bonding configurations, respectively.

3 Results and discussions

3.1 Effect of D_{cs} on a-Si:H film properties The defect density as a function of D_{cs} and the corresponding FTIR spectra were shown in Fig. 1 and Fig. 2, respectively.

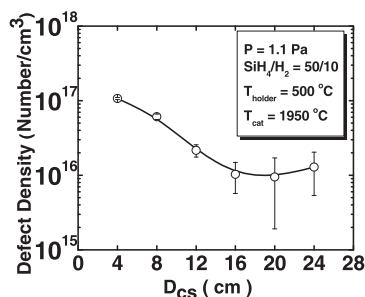


Figure 1 The influence of D_{cs} on the a-Si film defect density under high catalyzer temperature (1950 °C)

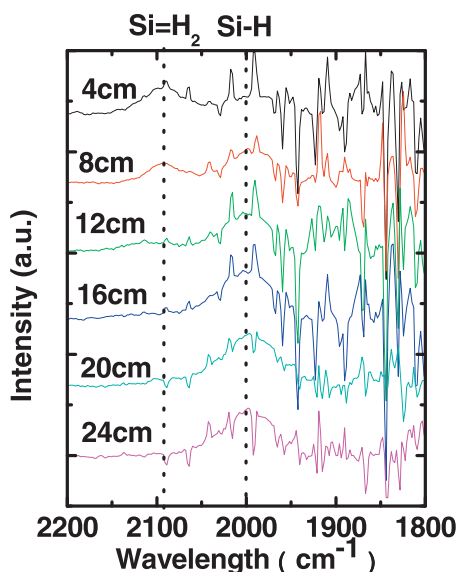


Figure 2 The FTIR spectrum of the a-Si films deposited at $T_{cat}=1950$ °C when varying the D_{cs} .

We found the D_{cs} to have a significant impact on the film quality. With increasing D_{cs} , the defect density decreases. The ratio of Si-H₂/Si-H bonding signals in infrared absorption spectra also decreases with increasing D_{cs} . The lower ratio indicates higher film quality. At a large D_{cs} of 24 cm, the Si=H₂ signal disappeared, and almost all the hydrogen is in the Si-H configuration, representing a better quality material.

3.2 Effect of pressure on a-Si:H film properties

The defect density as a function of deposition pressure (P), and its corresponding FTIR spectra were shown in Fig. 3 and Fig. 4, respectively.

For high- T_{cat} of 1950 °C, more defects were generated with increasing deposition pressure (P), which saturated as $P > 4$ Pa. In addition, the Si=H₂ signal at 2090 cm⁻¹ grew drastically, while the Si-H signal at 2000cm⁻¹ decreased as P was increased from 1.1 Pa to 8 Pa. In contrast, the defect density seemed insensitive to P at low- T_{cat} (1750 °C). The corresponding FTIR data showed consistent results. It was reported that more reactant species were generated at high- T_{cat} [6]. Therefore, a low deposition pressure is desirable for preparing good quality materials in order to minimize

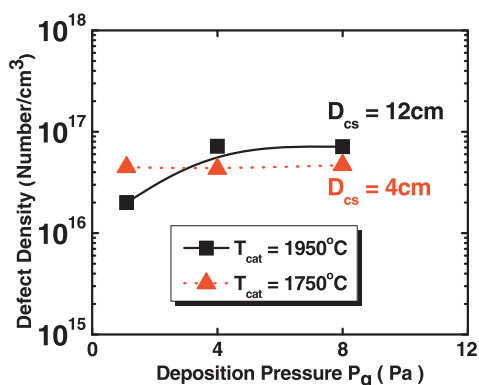


Figure 3 The ESR spin density as varying P at $T_{cat}=1950$ °C, $D_{cs}=12$ cm, and $T_{cat}=1750$ °C, $D_{cs}=4$ cm, respectively.

the gas phase reaction. In contrast, at low T_{cat} where the density of the Si-related species is low, the film quality is not sensitive to pressure within the range investigated.

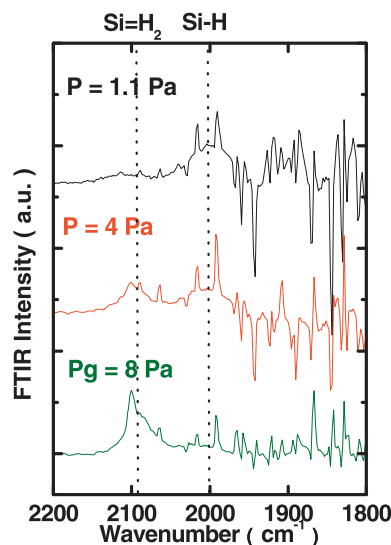


Figure 4 FTIR spectrum of the a-Si films deposited at $T_{cat}=1950$ °C, $D_{cs}=12$ cm, as a function of the P .

3.3 Dependence of a-Si:H film properties on catalyzer temperature (T_{cat})

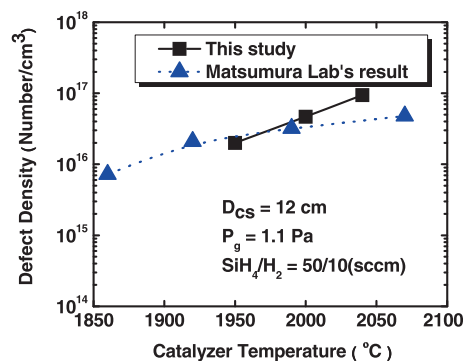


Figure 5 The ESR spin density vs. T_{cat} at $D_{cs}=12$ cm and $P=1.1$ Pa.

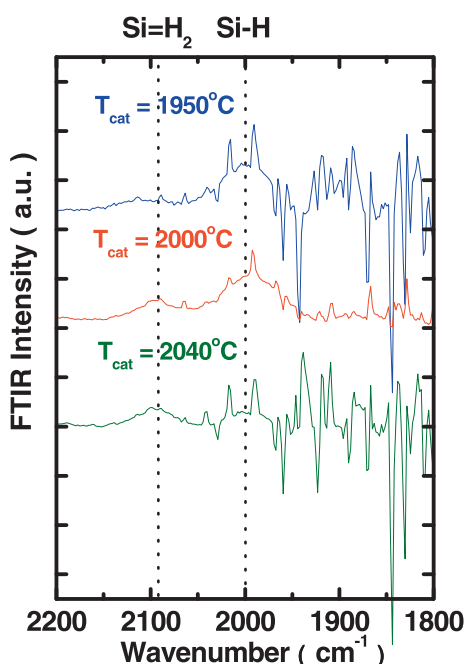


Figure 6 The FTIR spectra vs. T_{cat} at $D_{\text{cs}}=12$ cm and $P=1.1$ Pa.

As shown in Fig. 5, the defect density increased with increasing T_{cat} which is basically consistent with previous results obtained by Prof. Matsumura's group. Meanwhile, with increasing T_{cat} the Si=H₂ signal at 2090 cm⁻¹ increased at the expense of the Si-H signal, indicating that lower T_{cat} favors the formation of good quality materials (Fig. 6).

3.4 Dependence of a-Si:H film properties on SiH₄ and H₂ gas flows In order to examine the effects of SiH₄ flow rate on a-Si film quality, we deposited the a-Si:H films at SiH₄ flow rate of 50, 100, and 200 sccm, respectively. Observing from Fig. 7, the defect density significantly increased with the increase of SiH₄ flow. However, the corresponding FTIR spectra as shown in Fig. 8 indicated that the Si=H₂ signal and the Si-H signal stayed almost constant under various SiH₄ flow rate. In comparison, at low T_{cat} the defect density is insensitive to the SiH₄ flow rate.

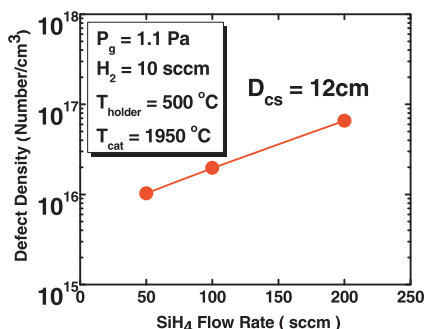


Figure 7 The ESR spin density vs. SiH₄ flow rate at $D_{\text{cs}}=12$ cm and $P = 1.1$ Pa, and $H_2 = 10$ sccm

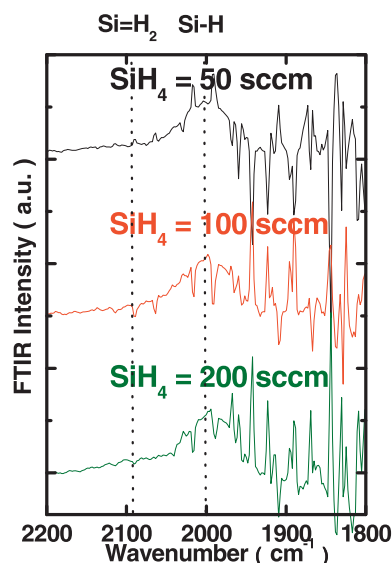


Figure 8 The FTIR spectra vs. SiH₄ flow rate at $D_{\text{cs}} = 12$ cm, $P = 1.1$ Pa, and $H_2 = 10$ sccm

It is interesting to note that the increase of defect density in a-Si:H film cannot be detected in FTIR in terms of the Si-H bonding configuration changes in the case of high- T_{cat} and large D_{cs} . Meanwhile, the deposition rate increased linearly with increasing SiH₄ gas flow rate, as shown in Fig. 9.

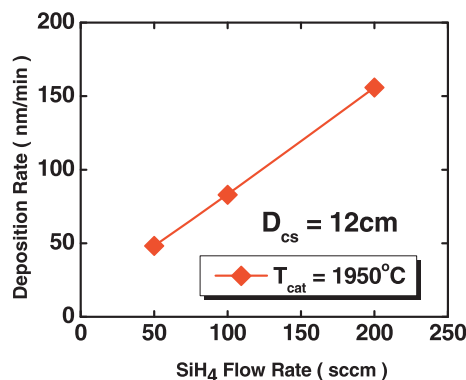


Figure 9 The dependence of deposition rate on SiH₄ gas flow rate.

In order to see if increasing the hydrogen presence in the gas phase can suppress the defect formation, we have varied the H₂ flow rate from 10 sccm to 40 sccm while the SiH₄ flow remained at 200 sccm. As shown in Figs. 10 and 11, we found that both the defect density and the FTIR spectra stayed almost unchanged, indicating that the H₂ flow is not effective in reducing the defect density. Meanwhile, as shown in Fig. 12, the deposition rate only slightly decreased as the H₂ flow was increased, indicating slight increase in etching associated with hydrogen.

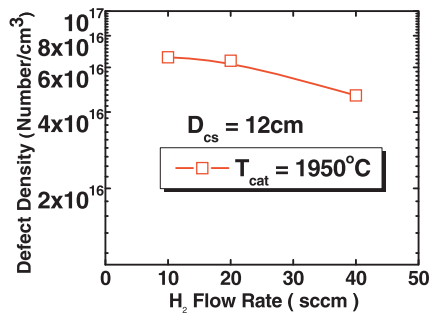


Figure 10 The ESR spin density vs. H_2 flow rate at $SiH_4 = 200$ sccm

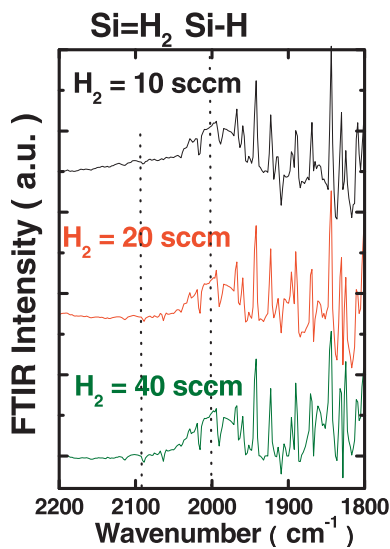


Figure 11 The FTIR spectra vs. H_2 flow rate at $SiH_4 = 200$ sccm

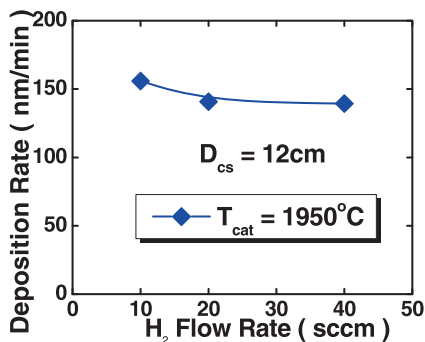


Figure 12 The deposition rate vs. H_2 flow rate at $SiH_4 = 200$ sccm

3.5 Thickness-dependence of defects in a-Si:H films In general, hydrogenated amorphous silicon prepared by plasma deposition at elevated temperature is not porous [7]. In order to separate the “bulk defects” from the “interface defects”, we deposited the a-Si:H films of different thicknesses under the condition of $T_{cat}=1950$ °C, $SiH_4/H_2=50/10$, and $P=1.1$ Pa. Using the same substrate area, the total number of the Si dangling bond defects as a

function of the deposition time for $D_{cs}=16$ cm and 24 cm were shown in Figs.13(a) and 13(b), respectively. The intercept at zero thickness provided information on the interface state density, which are 3.67×10^{12} for $D_{cs}=16$ cm and 2.20×10^{12} for $D_{cs}=24$ cm. These results correspond to an interface defect density of $1.22 \times 10^{12} \text{ cm}^{-2}$ for $D_{cs}=16$ cm and $0.73 \times 10^{12} \text{ cm}^{-2}$ for $D_{cs}=24$ cm.

On the other hand, the slope of the plot is proportional to the bulk defect density. We obtained a slope of 2.98×10^{12} for $D_{cs}=16$ cm, and 3.70×10^{12} for $D_{cs}=24$ cm. These results correspond to a bulk defect density of $1.14 \times 10^{16} \text{ cm}^{-3}$ for $D_{cs}=16$ cm and $1.42 \times 10^{16} \text{ cm}^{-3}$ for $D_{cs}=24$ cm.

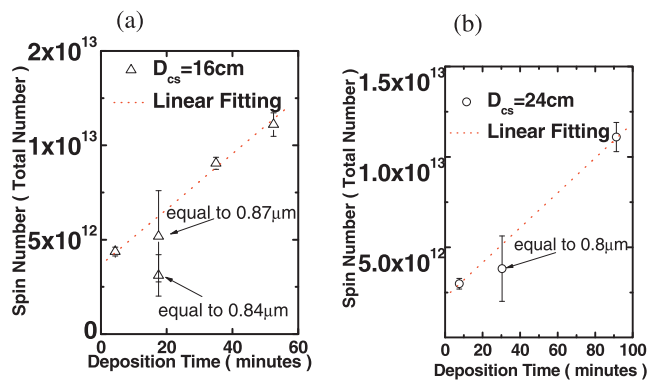


Figure 13 The ESR spin density vs. the deposition time.

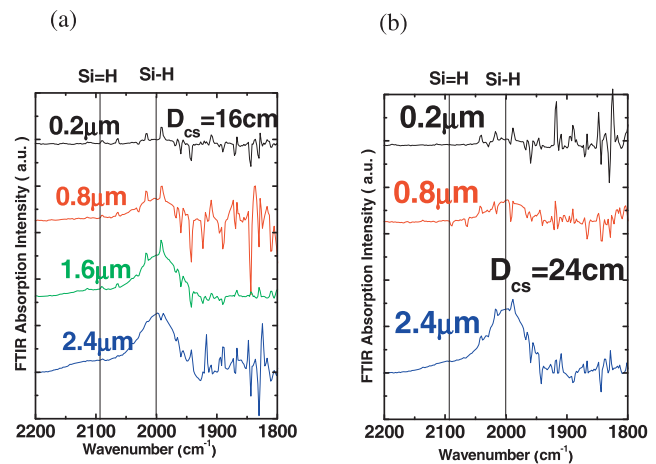


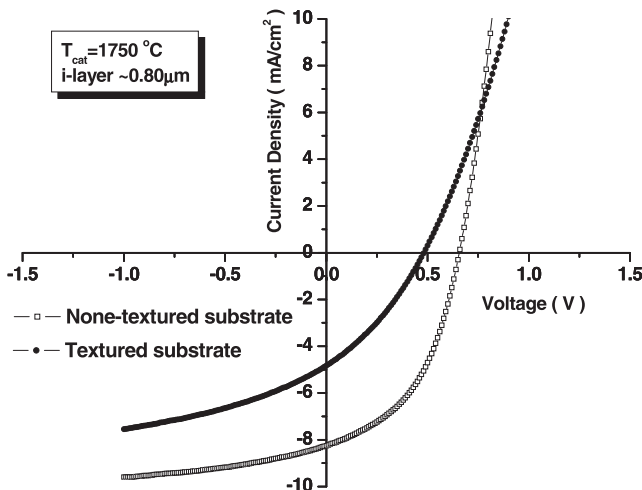
Figure 14 The FTIR spectra at different film thickness.

The FTIR spectra as a function of the film thickness were shown in Figs. 14(a) and 14(b) for $D_{cs}=16$ and 24 cm respectively. In both cases, the Si-H mono-hydride is the predominant bonding configuration independent of the film thickness. Nevertheless, there is still a small Si=H dihydride shoulder at 2090 cm^{-1} , which seemed more visible at the smaller D_{cs} of 16 cm.

3.6 Preliminary solar cell data Finally, in Fig. 15, we compared some preliminary results of solar cells on textured ($SnO_2:F$) and non-textured (ITO) substrates. It is

known that while textured TCO substrates can increase light trapping in a solar cell, improper texturing can also degrade the cell performance. For example, the shape of the TCO texturing can influence the a-Si:H film growth, and improper aspect ratio of the TCO groove can also result in defect formation in the a-Si:H film [8]. We found the solar cell performance degraded on textured substrate, which showed a larger shunt resistance (R_{shunt}) and lower series (R_{ser}) resistance.

In the series of experiment, we also utilized the high- T_{cat} (1850 °C and 1950 °C) deposited a-Si:H film as the solar cell intrinsic layer. It was found that the solar cell performance degraded with increasing T_{cat} , even when the high- T_{cat} a-Si:H film had a very low defect density as measured by ESR. The actual reason is still not clear. Further work is needed to gain a better insight on defects created in the high- T_{cat} a-Si:H films, and to understand the effect of TCO texturing on the defect generation in the Cat-CVD process.



	Voc (V)	Jsc (mA/cm ²)	FF (%)	Efficiency (%)
Textured	0.48	4.77	32.82	0.75
None-textured	0.656	8.25	45.77	2.48

Figure 15 Characteristics of solar cells on textured and non-textured substrates.

4 Conclusion In this study, the a-Si:H film properties and the solar cell characteristics were investigated under the high- T_{cat} regime in Cat-CVD. We found that although increasing the T_{cat} can degrade the quality of the a-Si:H, it is possible to obtain material with low defect density by employing process conditions of large D_{cs} , low silane flow rate, and low deposition pressure. We think it is important to suppress the gas phase reaction of the Si-related species during film growth in Cat-CVD in order to obtain good material in the high- T_{cat} regime. Further work is needed to evaluate the performance of solar cells using materials prepared under high T_{cat} conditions.

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