J Mater Sci (2006) 41:5287–5291
DOI 10.1007/s10853-006-0302-6

Quantitative hydrogen measurements in PECVD and HWCVD a-Si:H using FTIR spectroscopy

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Received: 4 August 2005 / Accepted: 7 October 2005 / Published online: 6 June 2006
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Abstract A series of hydrogenated amorphous silicon films have been deposited using plasma enhanced chemical vapour deposition (PECVD) and hot-wire chemical vapour deposition (HWCVD) techniques. The total concentration of bonded hydrogen in the films was varied between 3% and 18% as determined by hydrogen effusion measurements. Fourier transform infra-red (FTIR) spectra of the PECVD and HWCVD samples exhibit strong absorption peaks that correspond to Si–H bend and stretch modes, and Si–H_2 stretch modes. A quantitative fit of the FTIR peak areas to the hydrogen effusion concentrations reveals that there is reasonable agreement between the required proportionality constants in PECVD and HWCVD material for the Si–H bend and stretch modes. The uncertainty error for the FTIR proportionality constants is consistently greater for the HWCVD data set, however, which may indicate that the effective dynamical charge of the Si–H dipoles is perturbed in the HWCVD material by bonded impurities that are sourced from the tungsten wire.

Introduction

Hydrogenated amorphous silicon (a-Si:H) has been intensively studied as a technologically useful thin-film optoelectronic material over the past 40 years. The role of bonded hydrogen to optimise the photo-electronic properties of a-Si:H for device applications was appreciated by the mid-1970s when successful doping of the material was first demonstrated [1]. Controlled doping of a-Si:H from the gas phase resulted in the rapid development of devices for large area optoelectronics such as solar cells, photo-detectors and large area displays [2]. The preferred a-Si:H deposition method until the early 1990s was plasma enhanced chemical vapour deposition (PECVD) of silane (SiH_4) gas. However, to produce device quality a-Si:H using PECVD, the deposition rate must be kept low (≤ 1 Å s^{-1}) which may be commercially restrictive. Attempts to increase the PECVD deposition rate generally gives a greater concentration of bonded hydrogen, and an associated increase of internal strain in the a-Si:H bonding network. The higher internal strain results in a greater concentration of weak Si–Si bonds that give rise to undesirable metastable properties [3, 4]. Alternative deposition methods to the PECVD technique have therefore been developed over the past 10–15 years which attempt to significantly improve the a-Si:H deposition rate whilst maintaining acceptable level of bonded hydrogen and metastablity. A promising method of depositing such optimised a-Si:H films is hot wire chemical vapour deposition (HWCVD) [5, 6].

It is consequently important to have a convenient method of determining the total amount of bonded hydrogen in a-Si:H films. A simple (non-destructive) measurement is to record the infra-red spectrum of the silicon–hydrogen vibrational modes using a standard Fourier transform infra-red (FTIR) spectrometer. Quantitative analysis of the various absorption strengths in such FTIR spectra, compared to an independent estimate of the total concentration of bonded hydrogen, will allow proportionality constants to be determined for specific vibration modes. FTIR proportionality constants have previously

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been determined for PECVD a-Si:H [7, 8], but do not appear to have been reported for HWCVD a-Si:H. In the present work FTIR proportionality constants are therefore calculated for a series of a-Si:H samples deposited by the HWCVD method, and these magnitudes are compared with values determined using the same analysis procedure for a series of PECVD samples. The accuracy of the FTIR proportionality constants for both the HWCVD and PECVD data sets is evaluated, and implications concerning the local dynamical charge of Si-H dipoles for each deposition method are discussed.

Experimental details

The substrates used for all a-Si:H depositions were crystalline silicon wafers and chrome coated Corning 7059 glass. The crystalline silicon wafers were used for FTIR measurements, whereas the chrome coated 7059 glass substrates were used for hydrogen effusion measurements and to determine film thicknesses. The PECVD a-Si:H samples were deposited in a conventional reactor operating at 13.56 MHz and a power of 6.5 W. The SiH_4 flow rate was maintained at 40 sccm to give a chamber pressure of 150 mtorr. To systematically vary the amount of bonded hydrogen in the PECVD samples, substrate temperatures (T_s) were varied from 140 °C to 500 °C. A summary of the PECVD specimens deposited is given in Table 1. The HWCVD samples were grown in a radial flow reactor using a tungsten wire, 0.25 mm in diameter, which was nominally positioned 15 mm from the substrates. The tungsten filament temperature was held at 1500 °C as measured by an optical pyrometer. The SiH_4 flow rate in this case was maintained at 8 sccm to give a chamber pressure of 220 mtorr. The substrate temperature for the HWCVD depositions was varied over a more modest range between 200 °C and 350 °C. The amount of bonded hydrogen in the HWCVD films could not be systematically controlled by varying T_s as for the PECVD material, but was instead dictated by the deposition history of the filament and variations (±2 mm) of the nominal tungsten wire location from the filament [9]. A summary of the HWCVD specimens deposited is given in Table 1. The thicknesses of the PECVD and HWCVD films were measured from surface profiles of etched a-Si:H patterns on the 7059 substrates. The thicknesses that are given in Table 1 were then used to estimate the corresponding average deposition rates (R) from the known deposition times.

The FTIR spectra were recorded using a single beam Mattson 7000 spectrometer. Wavenumbers were scanned from 400 to 4000 cm^{-1} at a scan rate of 0.4 cm s^{-1}. During operation, the FTIR sample space was flushed continuously with zero-grade nitrogen to eliminate CO_2 and H_2O background absorptions from the recorded spectra.

Hydrogen effusion measurements were conducted using a propriety quartz chamber arrangement whose base operating pressure was typically 5×10^{-6} torr. A furnace was used to raise sample temperatures to a maximum of 850 °C at a linear heating rate of about 85 °C min^{-1}. The partial pressures of evolved H_2 from the a-Si:H films were monitored on a tuned Masstorr FX mass spectrometer. The total number of moles of specimen hydrogen detected at the mass spectrometer was calculated by comparison with the partial pressure signal from a standard hydrogen leak using the same pumping rate through the chamber. The percentage of hydrogen bonded by weight within the samples was finally enumerated from the measured sample volume and known density of a-Si:H [10, 11].

Results and discussion

Representative FTIR spectra that show the absorbance against wavenumber (υ) for a PECVD and HWCVD specimen are given in Fig. 1. Similar spectral features are present in both cases with strong absorbance peaks

Table 1 Summary of PECVD and HWCVD samples used for FTIR and hydrogen effusion measurements

PECVD					HWCVD				
Code	d (μm)	R (Å s^{-1})	T_s (°C)	C_H (%)	Code	d (μm)	R (Å s^{-1})	T_s (°C)	C_H (%)
PE1	1.02	0.9	500	3.1	HW1	0.29	1.4	350	11.9
PE2	1.43	1.0	390	5.2	HW2	1.45	8.1	350	9.2
PE3	0.92	0.9	310	7.4	HW3	0.50	2.8	300	12.7
PE4	1.30	0.9	280	8.8	HW4	1.10	6.1	300	10.5
PE5	1.50	1.0	240	11.9	HW5	1.40	7.8	275	15.4
PE6	2.11	1.9	200	12.2	HW6	2.00	11.1	250	12.8
PE7	1.80	1.6	200	12.2	HW7	1.30	7.2	250	10.0
PE8	1.84	2.0	180	13.6	HW8	1.00	5.6	200	18.3
PE9	1.55	2.4	160	14.8	HW9	1.75	9.7	200	13.9
PE10	1.24	2.8	140	18.0	HW10	1.35	7.5	200	14.3

The accuracy of T_s during a deposition run was ±3 °C for PECVD samples, and ±10 °C for HWCVD samples

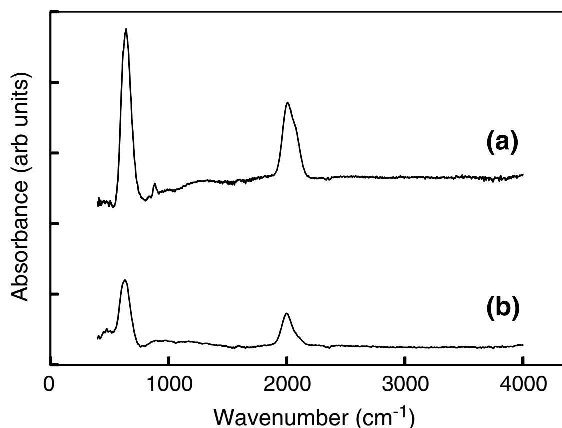

Fig. 1 FTIR spectra of PECVD and HWCVD a-Si:H in the as-grown state. (**a**) Sample PE6; C_H = 12.2%, (**b**) sample HW6; C_H = 12.8%

occurring at 640 cm^{-1}, and between 2000 and 2100 cm^{-1}. Absorption features specific to SiH_2 and SiH_3 bonding (860–890 cm^{-1}) were only detectable in PECVD and HWCVD samples which contained higher concentrations of bonded hydrogen (≥12% by weight) and were not quantitatively analysed. Quantitative analysis was instead focussed upon the strong peaks present in the Fig. 1 spectra. These features are associated with Si–H bonds that have a characteristic bend mode (640 cm^{-1}) and two stretch modes (2000 and 2090 cm^{-1}), and Si–H_2 bonds that have a wag mode (640 cm^{-1}) and a stretch mode (2095 cm^{-1}) [7, 12]. Analysis of these absorption features commenced by using a non-linear, quasi-Newton algorithm to perform Gaussian fitting to restricted wavenumber regions of the FTIR data. Gaussian fitting was performed at peak wavenumbers of 640, 2000 and 2095 cm^{-1} for all of the samples in Table 1. For any particular vibration mode, the total absorption strength is then found by simple numerical integration of the fitted Gaussian. The concentration of bonded hydrogen (C_H), which is assumed to be proportional to the overall density of absorbing Si–H or Si–H + Si–H_2 configurations, may then be found by integrating over appropriate mode lineshapes;

$$C_H = \frac{A_{\upsilon_o}}{d} \cdot \int_{-\infty}^{+\infty} \frac{G_{\upsilon_o}(\upsilon)}{\upsilon} d\upsilon \quad (1)$$

. In Eq. 1, d is the sample thickness, $G_{\upsilon_o}(\upsilon)$ is the fitted Gaussian lineshape centred at the vibrational mode wavenumber υ_o, and A_{υ_o} is an unknown proportionality constant. For the 640 cm^{-1} mode a single Gaussian integrated lineshape may thus be used to directly compute the associated proportionality constant (A_{640}). For other modes, where υ_o is specifically associated with either Si–H or Si–H_2 bonds (such as the 2000 cm^{-1} and 2095 cm^{-1} vibrations), a pair of lineshape integrals must be added to simultaneously determine the respective proportionality constants (A_{2000} and A_{2095}).

To experimentally determine the proportionality constants A_{υ_o} a calibration procedure was therefore performed where the total hydrogen concentration C_H was quantitatively determined for each sample by hydrogen effusion. Examples of typical effusion data for a PECVD and HWCVD specimen are given in Fig. 2 which shows the partial pressure of evolved hydrogen as a function of temperature. From these effusion graphs, the hydrogen is seen to evolve at a high temperature which is consistent with the thermal dissociation of monohydride Si–H bonds [13]. Only in the PECVD samples that were deposited at the lowest substrate temperatures (T_s < 200 °C), and in a subset of the HWCVD samples which contained larger amounts of hydrogen, was there evidence of a lower temperature effusion peak indicative of Si–H_2 dihydride configurations. The total hydrogen content measured for all of the PECVD and HWCVD samples are included in Table 1. The variation of C_H with T_s for the PECVD samples was found to exhibit Arrhenius behaviour with an activation energy of 0.14 eV which is consistent with a model of H_2 elimination from the growing a-Si:H surface [14]. Similar Arrhenius behaviour was not evident for the HWCVD films which may indicate the operation of a different growth mechanism. The calculated C_H values were estimated to be accurate to ±2% which mainly reflected the uncertainty associated with the integration procedure that was applied to the raw effusion signals.

Using the C_H magnitudes, FTIR proportionality constants were finally computed from Eq. 1. These values are given in Table 2 in the rows labelled A_{640}, A_{2000} and A_{2095}. The proportionality constants have been calculated using FTIR spectra taken immediately after the samples have been deposited, and also after the films have been annealed at 150 °C for 2 h in the dark to remove any metastable

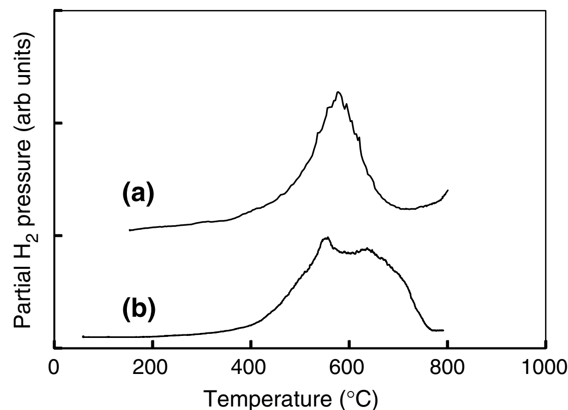

Fig. 2 Hydrogen effusion signals for PECVD and HWCVD a-Si:H in the as-grown state. (**a**) Sample PE4; C_H = 8.8%, (**b**) sample HW2; C_H = 9.2%

Table 2 FTIR proportionality constants for particular vibration modes in PECVD and HWCVD a-Si:H

IR Mode	υ_o (cm^{-1})	FTIR Constant	PECVD As-grown ($\times10^{19}$ cm^{-2})	PECVD Annealed ($\times10^{19}$ cm^{-2})	HWCVD As-grown ($\times10^{19}$ cm^{-2})	HWCVD Annealed ($\times10^{19}$ cm^{-2})
Si–H bend Si–H_2 wag	640	A_{640}	3.6 ± 0.2	3.8 ± 0.2	4.7 ± 0.4	4.4 ± 0.4
Si–H stretch	2000	A_{2000}	19.1 ± 0.8	19.9 ± 1.2	26.2 ± 3.0	18.5 ± 2.4
Si–H_2 stretch	2095	A_{2095}	20.4 ± 0.9	18.3 ± 1.1	9.0 ± 1.0	33.4 ± 4.4

states that are induced during initial handling. The proportionality constants computed for individual sample spectra exhibit some variation across both the PECVD and HWCVD sample sets for all three vibration modes. The optimum proportionality constants given in Table 2 were therefore obtained by performing a linear regression analysis upon the entire set of data for the PECVD and HWCVD samples. The regression procedure for the 2000 and 2095 cm^{-1} modes is illustrated in Fig. 3 for the PECVD and HWCVD samples in their as-grown and annealed states. For the Fig. 3 graphs, the hydrogen effusion values (taken to be fixed constants) are plotted against FTIR hydrogen estimates calculated from Eq. 1. The regression procedure optimises the FTIR A_{2000} and A_{2095} proportionality constants by minimising the overall sum of the squares of the differences between the effusion and FTIR magnitudes. Inspection of the Fig. 3 plots thus suggests that for the 2000 and 2095 cm^{-1} modes, quantitative hydrogen estimates using the optimised A_{2000} and A_{2095} constants will be more accurate for the PECVD compared to HWCVD samples. The associated error for the calculated A_{2000} and A_{2095} proportionality constants is consequently greater for HWCVD material compared to PECVD material. Similar conclusions are reached by performing a regression analysis for the 640 cm^{-1} mode.

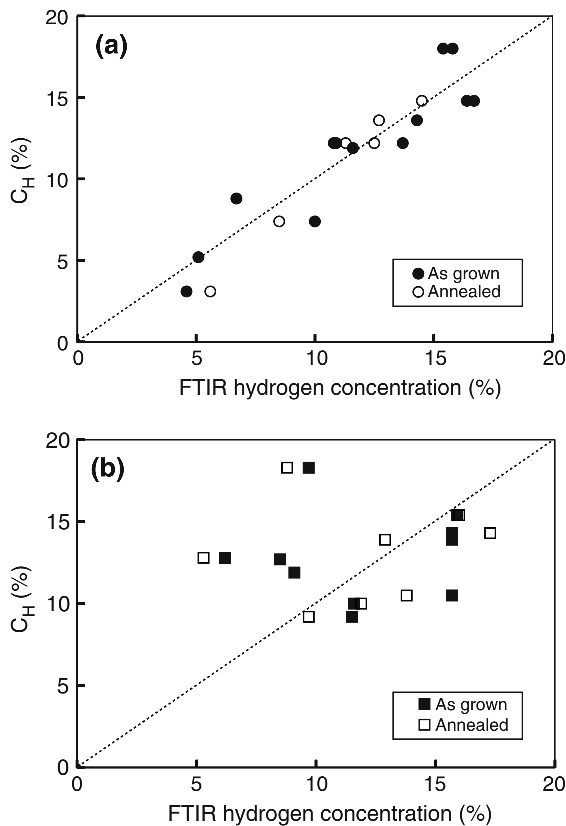

Fig. 3 Linear regression analysis to find the optimum FTIR proportionality constants A_{2000} and A_{2095}. The dashed line indicates equal amounts of hydrogen by the effusion and FTIR measurements and is a reference for the eye. (**a**) PECVD films (**b**) HWCVD films

Inspection of the PECVD proportionality constants in Table 2 reveals that, within the uncertainty errors quoted, there is reasonable agreement between the magnitudes found for all vibrational modes in either the as-grown or annealed states. Furthermore, the PECVD magnitudes found in the present work compare favourably with literature values for A_{640}, A_{2000} and A_{2095} [7, 8]. The PECVD proportionality magnitudes do not accordingly appear to be influenced by metastable states as previously reported for light-induced degradation studies [15]. There is less consistency between the as-grown and annealed proportionality constants for the HWCVD material, however, most noticeably for A_{2000} and A_{2095}, which may suggest that metastable states have a more critical influence for these samples.

With the exception of the Si–H_2 stretch mode, the magnitudes of the PECVD and HWCVD proportionality constants are found to be reasonably consistent within the calculated uncertainties. The error estimates for the HWCVD constants, particularly A_{2000} and A_{2095}, are larger than those found for the PECVD material, however, which suggests that the Si–H and Si–H_2 structural environment produced by different HWCVD depositions may be significantly different. Because the FTIR proportionality constants are fundamentally determined by the effective dynamical charge of the Si–H dipoles [7] they should be sensitive to changes in the local bonding environment. Defects and impurities in the deposited a-Si:H films are thus likely to influence the FTIR proportionality constants. For HWCVD films, previous work [9] has demonstrated that a potential source of oxygen and carbon contamination is out-gassing of the tungsten filament. The optoelectronic quality of HWCVD a-Si:H is thus sensitive to the age and

condition of the tungsten filament and this would also appear to be manifest in the greater uncertainty associated with the FTIR proportionality constants found in the present study. To achieve greater accuracy in HWCVD hydrogen estimates, quantitative FTIR measurements should thus preferably concentrate upon an analysis of the 640 cm^{-1} mode.

Conclusions

Quantitative hydrogen estimates may be made in PECVD and HWCVD a-Si:H films from FTIR spectra using appropriate proportionality constants for various Si–H and Si–H_2 vibration modes. The magnitudes of the proportionality constants are similar for Si–H bend and stretch modes in PECVD and HWCVD a-Si:H, but there is greater uncertainty associated with HWCVD hydrogen estimates. The greater uncertainty that underlies the HWCVD calculations may reflect variable impurity levels that are dictated by the deposition history of the tungsten filament.

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