

Infrared characterization of $a\text{-Si:H}/a\text{-Si}_{1-x}\text{C}_x\text{:H}$ interfaces

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Abstract

Infrared spectroscopy was used to characterize three series of $a\text{-Si:H}/a\text{-Si}_{1-x}\text{C}_x\text{:H}$ multilayers in which their geometrical parameters were varied. The infrared active vibrational groups in their spectra and the interference fringes in their absorption-free zone were studied to analyze the interfaces and the changes that are produced in very thin layers. Our results show that hydrogen is bonded to silicon only in monohydride groups. No additional hydrogen could be detected at these interfaces. The deposition of very thin $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ layers seems to affect their porous structure, making them denser.

1. Introduction

Amorphous silicon-based multilayers have been extensively studied during the last decade. In addition to their intrinsic interest because of their properties and their claimed and discussed quantum effects and their possible application to devices, these materials provide a powerful tool to study the interfaces between amorphous silicon alloys.

One of the more interesting types of interface is that between hydrogenated amorphous silicon ($a\text{-Si:H}$) and hydrogenated amorphous silicon-carbon alloys ($a\text{-Si}_{1-x}\text{C}_x\text{:H}$). This interface is very common in $a\text{-Si:H}$ solar cells where $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ is used as a window layer because of its wide bandgap, which enhances the spectral response at lower wavelengths [1].

The H in $a\text{-Si:H}/a\text{-Si}_{1-x}\text{C}_x\text{:H}$ multilayers has not been extensively studied and, except for a paper from Yoshimoto and Matsunami [2], only casual references to the presence of additional H at the interfaces [3,4] are reported. As far as H bonding is concerned, the identification of the H bonding state is not straightforward due to the overlap of several contributions in the Si-H stretching band. In particular, the contribution around $2070\text{-}2090\text{ cm}^{-1}$ can be attributed to Si-H_n ($n>1$) groups [5], to Si-H groups on inner surfaces [6] or to Si-H bonds in the proximity of C atoms [7].

In addition to the H incorporation scheme in these structures, another important issue is whether the thicknesses of the layers at the nanometer scale could modify the structure of the same material in homogeneous and thicker films (in the micron scale). This is particularly interesting in the case of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films which have been reported to present a porous structure when their carbon content is high (i.e. when their bandgap is wider and, consequently, more interesting optical properties are presented) [8,9].

In this paper we present an exhaustive study on these interfaces by using infrared

spectroscopy (IRS). Three series of a -Si:H/ a -Si_{1-x}C_x:H multilayers with the same base materials were used to study the H bonded in these interfaces.

2. Experimental procedures

2.1. Sample preparation

Three series of a -Si:H/ a -Si_{1-x}C_x:H multilayers were deposited in an RF capacitively coupled reactor with an automated substrate holder, as described elsewhere [10]. All the samples were prepared at a substrate temperature of 300°C and an RF (13.56 MHz) power of 5 W (27 mW cm⁻²). The gas pressure was maintained at 20 Pa, and pure silane (20 sccm) and a mixture of silane (1 sccm) and methane (19 sccm) were respectively used in a -Si:H and a -Si_{1-x}C_x:H deposition. The plasma was maintained during the gas switching process, but substrates were removed from plasma influence until conditions were stable [10]. The carbon content (x) in a -Si_{1-x}C_x:H alloys was found to be 0.36 by X-ray photoelectron spectroscopy (XPS).

Two series with variable mean composition (labeled A and B) and a series with constant mean composition (labeled C) were prepared. The number of elementary layers was varied, but the thickness of the multilayers was always kept around 0.5 μm. In series A, the a -Si:H layer thickness (d_{Si}) was varied and the a -Si_{1-x}C_x:H layer thickness (d_{SiC}) was kept at 37 Å, and in series B d_{SiC} was changed by keeping d_{Si} at 55 Å. In series C, both thicknesses were changed by the same ratio, and total thickness of the multilayers was kept constant. In Table I, we present the thicknesses and number of elementary pairs of layers for the samples studied. The structure of the multilayers was studied in a previous paper [10], showing a very good periodicity, but non-

strictly abrupt interfaces with a thickness of around 10 Å. The samples were deposited onto intrinsic crystalline silicon wafers.

2.2. IRS characterization and data analysis

These multilayers and a homogeneous film of each of the two materials used in multilayers were characterized by Infrared Spectroscopy in a BOMEM DA3 spectrometer in the range between 400 and 4000 cm^{-1} . The spectra were acquired in the normal incidence geometry, under vacuum, and with a 4 cm^{-1} resolution.

In order to obtain the absorption spectra of the samples, we measured the transmittance of the substrate ($T_S(\nu)$) with the residual atmosphere spectrum as reference, the transmittance of the film/substrate system with the residual atmosphere spectrum as reference ($T_{F/V}(\nu)$), and the transmittance of the film/substrate system with the substrate spectrum as reference ($T_{F/S}(\nu)$). The spectrum $T_{F/S}(\nu)$ was divided by $T_S(\nu)$ to eliminate the absorption contribution due to the substrate. The resulting spectrum was then normalized by multiplying it by the mean value of the $T_S(\nu)$ in the zone where no absorption bands are present. The result of this treatment ($T(\nu)$) is compared to $T_{F/V}(\nu)$ and should be nearly identical except for the zone where there are absorption bands due to substrate. The absorption spectra were obtained by fitting the zones in $T(\nu)$ that did not present absorption bands with the theoretical expression corresponding to the transmittance of a non-absorbing film with an index of refraction n (which is considered constant in this range), a thickness d , onto a semi-infinite substrate with an index of refraction s :

$$T_0(\nu) = \frac{A}{B - C \cos(4\pi \nu nd) + D} \quad (1)$$

where: $A = 16 n^2$

$$B = (n + 1)^3 (n + s^2)$$

$$C = 2 (n^2 - 1) (n^2 - s^2)$$

$$D = (n - 1)^3 (n - s^2)$$

These fits allow us to obtain the values of the parameters n , d and s . From these values the absorption spectra ($\alpha(\nu)$) are calculated from the $T(\nu)$ expression:

$$T(\nu) = \frac{Ax}{B - Cx \cos(4\pi \nu nd) + Dx^2} \quad (2)$$

where $x = e^{-\alpha d}$, and A , B , C and D are as previously calculated from the fits.

The H content bonded to silicon and carbon atoms in our samples was calculated from the integration of the Si-H_n and CH_n stretching bands:

$$N_H (\text{cm}^{-3}) = K \int_{\text{band}} \frac{\alpha(\nu)}{\nu} d\nu \quad (3)$$

where K was taken as $1.4 \times 10^{20} \text{ cm}^{-2}$ for the Si-H_n stretching band and $1.0 \times 10^{21} \text{ cm}^{-2}$ for the CH_n stretching band [1]. Although these K values are arbitrary and no calibration was performed to our films with other techniques they are orientative and useful for comparison purposes.

3. Results and discussion

The $T(\nu)$ spectra corresponding to the base materials used in the multilayers are presented in figure 1. The a -Si:H spectrum shows only two significant bands, the Si-H stretching one (centered at 2000 cm^{-1}) and the rocking one (centered at 630 cm^{-1}). The absence of contribution around 2090 cm^{-1} in the stretching band suggests that no Si-H_n ($n>1$) bonds are present and that the material is dense, without microvoids. The a -Si_{1-x}C_x:H film presents other characteristic bands

of this material: the CH₃ stretching band (2890-2940 cm⁻¹), the Si-CH₃ bending band (1250 cm⁻¹), the CH₃ bending band (1350-1400 cm⁻¹) and the rocking and wagging bands of the Si-CH₃ group (780 cm⁻¹). In addition, the stretching Si-H_n band is located around 2090 cm⁻¹, without any significant contribution at 2000 cm⁻¹. The absence of significant bands in the range 860-890 cm⁻¹ suggests that no Si-H₂ groups are present. Thus the contribution at 2090 cm⁻¹ should be due to Si-H bonds in microvoids or to Si-H bonds with C atoms in their vicinity. The higher absorption of this band in *a*-Si_{1-x}C_x:H layer is due to the higher porosity of this material, as deduced from previously published results on the thermal desorption spectroscopy of *a*-Si_{1-x}C_x:H films with a similar C content [8].

The fit of the spectra in the absorption-free zone for these samples gives a refraction index of 2.99 for *a*-Si:H and 1.75 for *a*-Si_{1-x}C_x:H. From the $\alpha(\nu)$ spectra we have calculated the H content bonded to silicon through equation (3) applied to the Si-H_n stretching band, and 4.7×10^{21} cm⁻³ and 1.2×10^{22} cm⁻³ were respectively obtained for *a*-Si:H and *a*-Si_{1-x}C_x:H films. The H content bonded to carbon atoms in the alloy was estimated to be 7.4×10^{21} cm⁻³ by the same method applied to the CH₃ band. This amount is around 40 % of the H present in the alloy, which is nearly the same percentage as that found for carbon content. This suggests that H has no significant preference for Si or C atoms.

The $T(\nu)$ spectra corresponding to the series A and B, both with variable mean composition, are presented in figures 2 and 3. The first feature that stands out in these spectra is the shape of the absorption-free transmittance spectra. The samples which presented a lower mean carbon content showed softer interference fringes due to the smaller difference between the mean index of refraction of the multilayer and that of the silicon substrate. This mean index of refraction can be calculated through the following expression [11]:

$$n_M^2 = n_{Si}^2 \frac{d_{Si}}{d_{Si} + d_{SiC}} + n_{SiC}^2 \frac{d_{SiC}}{d_{Si} + d_{SiC}} \quad (4)$$

The absence of any noticeable absorption band in the range 860-890 cm^{-1} (corresponding to Si-H₂ bending band) suggests that no Si atoms are bonded to more than one H atom. This leads to the conclusion that all the 2090 cm^{-1} contribution in Si-H stretching band is due to H atoms on the inner surfaces of microvoids or to Si-H bonds in the neighbourhood of C atoms (in the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloy or in the $a\text{-Si:H}$ layers near the interfaces). From the results corresponding to the reference materials, we can conclude that the transmittance spectra of these multilayers are between those of the reference materials, and that the multilayer structure does not significantly influence the spectra. The calculation of the content of H bonded to Si atoms in these multilayers through equation (3) shows that this depends only on the mean composition of the multilayer. The H content as a function of the mean C content is plotted in figure 4. This mean C content was calculated from the nominal thicknesses of the elementary layers and assuming the same C content in the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ layers that in homogeneous films. The H contents of the multilayers are distributed along the line that connects the contents of the reference materials. Similar behavior was observed for the H bonded to C atoms, but the scatter of the data is much higher due to the lower absorption of the CH stretching band and the difficulty in the accurate determination of the $\alpha(\nu)$ spectra from the transmittance spectra.

In order to perform a more detailed analysis of the possible influence of the multilayer structure on the absorption spectra, we have synthesized the expected absorption spectra from the experimental spectra of the reference materials through the following equation [11]:

$$\alpha_M = \alpha_{Si} \frac{n_{Si}}{n_M} \frac{d_{Si}}{d_{Si} + d_{SiC}} + \alpha_{SiC} \frac{n_{SiC}}{n_M} \frac{d_{SiC}}{d_{Si} + d_{SiC}} \quad (5)$$

The comparison between the synthesized spectra and the experimental ones did not show

significant differences in the shape of the curves. Nevertheless, a slight increase in the integrated area of the experimental spectra of all the samples was observed, but no correlation between this increase and the number of interfaces in the multilayers was found. This suggests that the amount of additional H atoms which could be present at the interfaces should be very small. In fact, some authors have estimated this amount to be of the order of 10^{14} cm^{-2} [3]. This amount is, in our opinion, too small to be detected in our multilayers. In the sample A6, which presents the highest number of elementary pairs of layers, this amount would mean an additional density of H atoms of around $4 \times 10^{20} \text{ cm}^{-3}$, which is less than 5% of the total H density.

The effective index of refraction of the multilayers obtained from the fit of $T_0(\nu)$ can be used to deduce the index of refraction of the reference materials, by fitting equation (4). In figure 5 the effective index for the multilayers of series A is presented as a function of the varying thickness. The data were fitted by using n_{Si} and n_{SiC} as parameters, and the best fit is also plotted in this figure. The values of these parameters were 2.99 for n_{Si} and 1.84 for n_{SiC} . The n_{Si} value is within the experimental error equal to that obtained for a $a\text{-Si:H}$ layer (2.99), whereas that of n_{SiC} obtained from the fit significantly differs from the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ layer used as reference (1.75). This difference could be due to the lower incorporation of C or H in the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ layers when they are in a multilayer structure, or to a reduction of the microvoids in the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ when the thickness of the layers is very small (37 Å in this series). Both explanations would imply an increase in the density of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ and, consequently, an increase in the refraction index. However, the H content in the multilayers is nearly the same as that corresponding to a homogeneous film with identical mean composition as deduced from figure 4, and no differences in the C incorporation with respect to homogeneous films are expected due to the multilayer deposition process, where self bias voltage during the deposition of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ layers was identical to the one measured during deposition of homogeneous films [10]. In our opinion, these

facts suggest that the change of the microstructure of the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ when it is arranged in a very thin layer is the most plausible explanation for the increase of the density. This change could be due to the thinness of the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ layers, which prevents the growth of large microvoids. The growth of $a\text{-Si:H}$ layers on top them partially fills these growing microvoids, giving non-abrupt interfaces, but also a low density of dangling bonds [12] and a higher density of the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ layers as a result.

Clarification about the presence of additional H at the interfaces could be expected from our experiments on series C, where the mean composition was kept constant, and only the thicknesses and number of elementary pairs of layers were varied. The transmittance spectra of the multilayers of series C are presented in figure 6. The first feature that should be noticed is that the shape of the absorption-free zone in the spectra is identical in all samples, suggesting that the effective refraction index does not change. This could be expected from equation 4. The H bonded to C atoms does not change when the number of interfaces increases. The most important difference among these spectra comes from the Si-H stretching band. The 2090 cm^{-1} contribution increases when the thicknesses of the elementary layers decrease, whereas the total amount of H in this band does not change significantly. This fact is more evident in the absorption spectra of these samples, which is presented in figure 7. There is no systematic increase in the H content in the samples to suggest the presence of additional H at the interfaces. The increase in the 2090 cm^{-1} contribution is due to the fact that the density of Si-H bonds in the vicinity of C atoms increases when the layers are thinner. This interpretation would also be consistent with the shape of the Si-H stretching band of samples A1, A2 (figure 2) and B4 (figure 3). Whereas the three samples presented very similar average carbon contents, the sample B4 ($x_{avg} = 0.05$), which consists of 80 elementary pairs of layers, shows a more pronounced 2090 cm^{-1} contribution than the samples A1 ($x_{avg} = 0.04$) and A2 ($x_{avg} = 0.07$), which respectively consist of 15 and 25

elementary pairs of layers.

4. Summary and conclusions

From the IRS analysis of three series of a -Si:H/ a -Si_{1-x}C_x:H multilayers and the base materials used in them, we can conclude that H is bonded to Si atoms only in monohydride groups. Although the H content is higher in a -Si_{1-x}C_x:H layers due to their porous structure, no preference for Si or C atoms was detected. The H content in the multilayers correlates well with their mean composition, showing an intermediate behavior between that of the two base materials, and no additional H was detected at the interfaces.

An increase in the 2090 cm⁻¹ contribution of the Si-H stretching band was observed when the average carbon content is increased, and also in samples with similar average carbon contents when the number of interfaces is increased (i.e. the elementary layers are thinner). The analysis of the absorption-free zone of the spectra of the multilayers with variable mean composition allowed us to obtain their effective refraction index and to deduce the index of the base materials. The refraction index of the a -Si_{1-x}C_x:H layers with low thicknesses deduced in this way is higher than that deduced from homogeneous films. This suggests that the a -Si_{1-x}C_x:H layers in multilayers present a denser structure. Thus, the rise in the 2090 cm⁻¹ contribution when the number of interfaces is increased should be attributed to the Si-H bonds in the vicinity of C atoms.

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Figure captions

- Figure 1.** Infrared transmittance spectra corresponding to the two base materials used in the multilayers.
- Figure 2.** Infrared transmittance spectra corresponding to the multilayers of the series A, which presented a variable mean composition and a constant thickness of the elementary $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ layers. The first number indicates the number of elementary pairs of layers, and the numbers parenthesized are respectively the thickness of $a\text{-Si:H}$ and $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ in Å.
- Figure 3.** Infrared transmittance spectra corresponding to the multilayers of the series B, which presented a variable mean composition and a constant thickness of the elementary $a\text{-Si:H}$ layers. The convention in the description of the multilayers is the same that in Fig. 2.
- Figure 4.** Hydrogen bonded to silicon density as a function of the average carbon content of the multilayers with variable mean composition (series A and B). The same values for the two base materials are plotted. The dashed line is just for connecting these two points.
- Figure 5.** Effective index of refraction of the multilayers of series A as a function of the thickness of the $a\text{-Si:H}$ layer. From the fit, the values of n_{Si} and n_{SiC} are obtained.
- Figure 6.** Infrared transmittance spectra corresponding to the multilayers of the series C, which presented a constant mean composition. The convention in the description of the multilayers is the same that in Fig. 2.
- Figure 7.** Absorption spectra of the Si-H stretching band corresponding to the multilayers of the series C.

Table I. Multilayers used in this study. d_{Si} and d_{SiC} are respectively the thicknesses of a -Si:H and a -Si_{1-x}C_x:H layers and N is the number of elementary pairs of layers.

Sample	d_{Si} (Å)	d_{SiC} (Å)	N
A1	263	37	15
A2	147	37	25
A3	73	37	40
A4	30	37	60
A5	18	37	80
A6	7	37	100
B1	55	205	20
B2	55	75	40
B3	55	32	60
B4	55	9	80
C1	156	195	15
C2	60	67	40
C3	30	35	80













