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The valence band structure of a-Si_{1-x}C_x:H studied by x-ray emission spectroscopy

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Abstract. The x-ray Si K-emission bands of a series of amorphous hydrogenated silicon-carbon alloy films (a-Si_{1-x}C_x:H, 0 ≤ x ≤ 0.78) and of crystalline Si and SiC (α-SiC and β-SiC) have been measured. The films have been prepared by plasma decomposition of mixtures of silane and methane. Up to x ≈ 0.5 the Si K-emission band exhibits only small changes indicating that few Si–C bonds have been formed and that, in consequence, each carbon remains bound to several hydrogen atoms. At higher carbon content (x = 0.62) the spectrum alters markedly and reveals features characteristic of tetrahedrally coordinated SiC. These features are still retained at x = 0.78 although additional broadening occurs for low-lying valence states. It is concluded that up to a fairly high concentration of carbon (x = 0.47) the network is dominated by Si–Si bonds, a conclusion further supported by Raman data. This Si-based network destabilises in a narrow range of composition, and Si–C bonds become essential in the formation of the network.

1. Introduction

In a recent study of hydrogenated methane-based Si–C films Sotiropoulos and Weiser reported measurements of the optical constants in the energy range up to 10 eV derived from a Kramers–Kronig analysis of reflectance data [1, 2]. They found that the properties change only gradually for compositions up to x = 0.47, retaining the features typical for a-Si:H, such as the steepness of the absorption edge and the position of the peak of the spectrum of ε₂, the imaginary part of the dielectric function. These features are lost rather abruptly with further rise in the carbon content. Since the optical properties are closely related to film composition and chemical bonding these changes reflect pronounced alterations of the local structure and bonding properties within a narrow range of composition near x = 0.5.

These results disagree with those obtained in a study by Mui and co-workers [3, 4] on ethylene-based Si–C films in which the optical constants were derived from ellipsometry in an energy range of 1.5 to 4.75 eV. Mui and co-workers reported a gradual change of the optical properties with composition, including a shift of the ε₂-peak without abrupt changes near x = 0.5.

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It is well known that the physical properties of a-Si:H and its alloys depend critically on deposition parameters (a-Si:H [5, 6], a-C:H [7–9], a-Si_{1-x}C_x [10, 11]). Therefore the differences between the optical properties reported by the two groups may be due to different preparation conditions. The analysis of the data, on the other hand, requires either an extrapolation of the reflectivity beyond the experimentally accessible range or depends on the assumption that the surface of the sample is smooth, homogeneous and uncontaminated (ellipsometry). It therefore seemed worthwhile to study the structural changes in the alloys with rising carbon content by applying x-ray spectroscopy as an experimental method that is quite different from the determination of optical properties.

X-ray emission bands arising from electron transitions from the valence band to empty core states can be used to probe the local environment of an atom and are closely related to the local partial density of states (DOS). They are therefore sensitive to changes in the local geometry and the bond character. Si K-emission bands reflect Si p-like states; Si L- and C K-emission bands reflect Si (s + d)- and C p-like states, respectively. X-ray emission spectroscopy therefore directly probes the bonding states and may serve as an independent method for studying the electronic structure of a-Si_{1-x}C_x:H alloys, complementary to the optical data method.

In this paper we report measurements of the x-ray Si K-emission bands, transitions between valence band states and the Si 1s core state, for films with composition up to $x = 0.78$. For comparison, the Si K-emission bands of crystalline silicon and of α - and β -SiC were also measured. The conclusions concerning changes of the local bonding were further compared with Raman data obtained on identical samples.

2. Experimental details

The samples of a-Si_{1-x}C_x:H were prepared by plasma deposition in a capacitatively coupled discharge from undiluted mixtures of silane and methane. Details of the sample preparation and sample parameters are described in a report of the study of their optical properties [1]. Films about 1 μm thick were grown on molybdenum substrates held at 250 °C. Their size was 8 \times 24 mm². Special care was taken to avoid oxygen in the discharge chamber; the samples were, however, exposed to air before the x-ray spectra were taken.

The Si K-emission bands were recorded in a Johann-type spectrometer held under a pressure of less than 10⁻⁵ Torr. Fluorescence excitation was used (tungsten anode: 10 kV, 200 mA) which is less destructive than excitation by electron bombardment [12]. The samples were mounted on a water-cooled sample holder which kept the temperature of the films during exposure below 30 °C. The dispersing element was a quartz crystal cut parallel to 10 $\bar{1}0$ and bent to a radius of 108 cm. The temperature of the crystal holder was kept constant within ± 0.05 °C at about 29 °C. The detector was a recently developed position-sensitive gas proportional counter with backgammon geometry of one of the two cathodes. The lateral resolution is better than 200 μm , corresponding to an energy resolution in the range of Si K-emission of about 0.5 eV.

Data acquisition was accomplished by a microprocessor system. By using the position-sensitive detector a factor of 10 to 20 was gained as compared with conventional step scanning. In the maximum of the spectra about 30 000 net pulses were accumulated within 20 to 70 h, depending on sample thickness and composition.

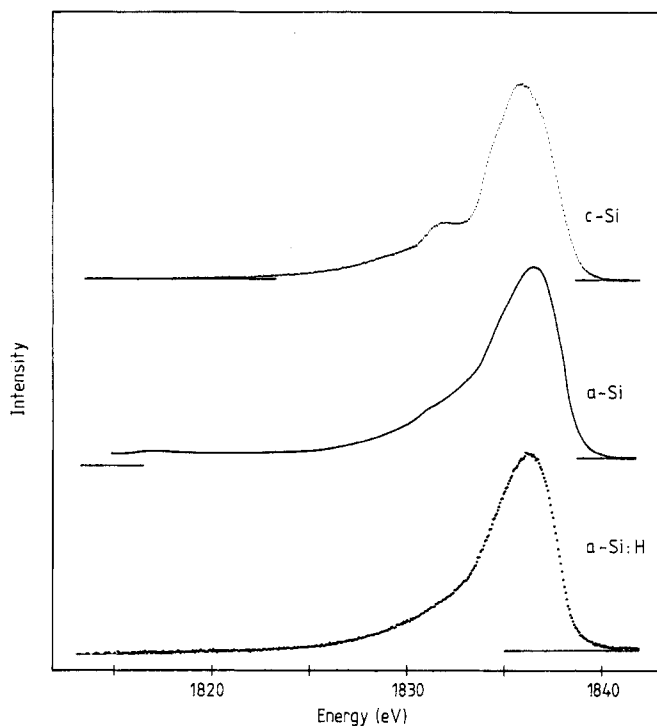


Figure 1. A comparison of Si K-emission bands of crystalline silicon (c-Si) and amorphous silicon prepared by evaporation (a-Si) or by plasma deposition (a-Si:H).

Raman spectra were excited with an argon laser (2.41 eV) and measured with a 0.85 m double-grating spectrometer followed by a third monochromator and a photon-counting system.

3. Results

3.1. Si K-emission bands of a-Si, a-Si:H and c-Si

The K-emission bands of crystalline silicon (c-Si), evaporated silicon (a-Si) and plasma-deposited Si (a-Si:H) are shown in figure 1. The Si K-emission bands of a-Si and a-Si:H exhibit smooth and highly asymmetric intensity distributions with a steep slope on the high-photon-energy side; to the low-energy side the intensity decreases monotonically with a change in slope at about 1833 eV. The extrapolation of the linear part of the high-energy edge may be considered as the top of the valence band. The loss of structural details is characteristic of the spectra of amorphous materials. However, on the whole the intensity of distributions follow those of their crystalline counterpart.

Closer inspection of the data reveals some differences. The main peak of the K-emission band in a-Si [13] is shifted by 0.5 eV to higher photon energy as compared to c-Si where the peak is found at 1836.0 eV, thus yielding a steeper high-energy edge. The FWHM is broader in the amorphous sample, 4.2 eV for a-Si and 3.75 eV in c-Si. In going from a-Si to a-Si:H some changes are observed too: the peak has shifted by 0.2 eV to lower energy, to 1836.4 eV, closer to the peak of c-Si; the high-energy edge has shifted

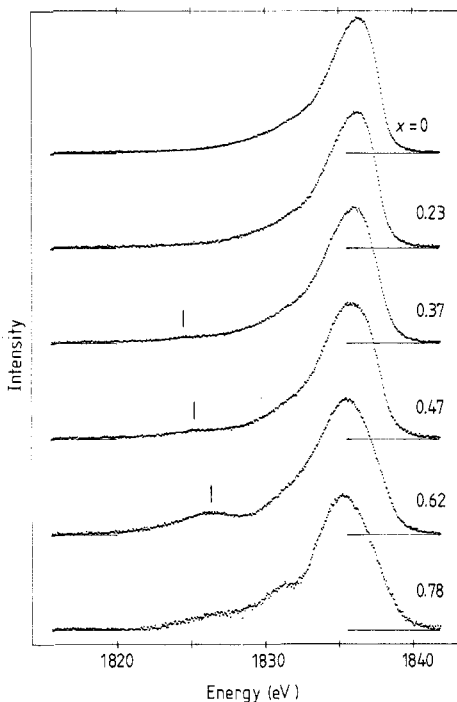


Figure 2. Si K-emission bands of a-Si_{1-x}C_x:H alloy films of various compositions. The spectrum for $x = 0.78$ has been corrected for some silicon-oxygen component; for the original spectrum see figure 3.

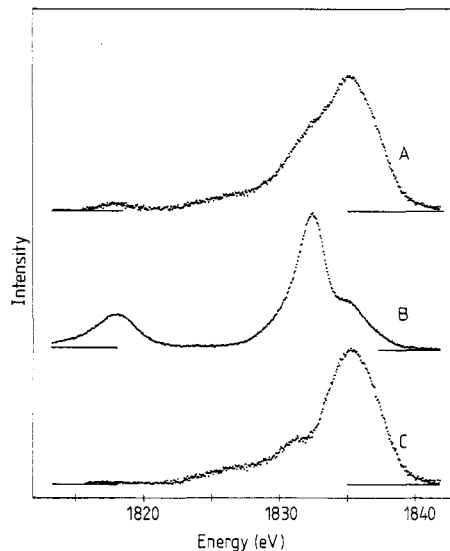


Figure 3. Si K-emission bands of (A) carbon-rich a-Si_{1-x}C_x:H films ($x = 0.78$, original measurement) and (B) quartz, and (C) a difference spectrum. For details, see the text.

to lower energies by 0.2–0.3 eV and the FWHM has decreased to 3.95 eV. On the low-energy side the spectra are almost identical.

The sample of a-Si contained some oxidised silicon (less than 5%) which modifies the spectrum and leads to some uncertainty in the range near 1832 eV. Correcting the spectrum for oxygen contributions would slightly reduce the intensity in this range, thus yielding approximately the same intensities for both amorphous samples.

Incorporation of hydrogen into amorphous Si causes a shift of the peak of the spectrum and its high-energy edge. The same trends were found by Senemaud and co-workers [14, 15] although their spectra differ from ours somewhat, showing on the low-photon-energy side a larger intensity for a-Si than for a-Si:H (about 50%) and larger linewidth (a-Si: ≈ 4.4 eV; a-Si:H: ≈ 4.1 eV).

3.2. Si K-emission bands of a-Si_{1-x}C_x:H

The Si K-emission bands of a-Si_{1-x}C_x:H for various compositions are shown in figure 2. The spectra are the original data corrected only for a linear background, except for the most carbon-rich sample ($x = 0.78$) where a small contribution of oxygen has been subtracted.

As shown in figure 3 the emission of the sample with $x = 0.78$ exhibits a small peak at low energy around 1818 eV characteristic for Si–O bonding. It originates from O 2s-derived states and is present in the x-ray spectra of oxides [16, 17]. After this feature had

Table 1. The peak position E_p and half-width FWHM of Si K-emission bands of a- $\text{Si}_{1-x}\text{C}_x\text{:H}$ alloy films for various compositions x .

| x | E_p (eV) | FWHM (eV) |
|------|-------------------|-----------------|
| 0 | 1836.4 ± 0.05 | 3.95 ± 0.05 |
| 0.23 | 1836.3 | 4.05 |
| 0.37 | 1836.0 | 4.30 |
| 0.47 | 1835.8 | 4.50 |
| 0.62 | 1835.5 | 5.10 |
| 0.78 | 1835.2 | 4.75 ± 0.1 |

been noticed a new sample was prepared, carefully avoiding oxygen during deposition, which is slow for carbon-rich samples. Despite these precautions the feature showed up again. It appears that films with such large carbon content are particularly susceptible to oxygen, which has probably entered while the sample was exposed to air. This may indicate a rather open network of Si, C and H atoms in this film. The susceptibility to oxygen seems to be limited to the carbon-rich samples because the spectra of all other samples, including that with the composition $x = 0.62$, did not show any sign of oxidation.

In many silicates and in vitreous silica the intensity of this oxygen-related feature reaches 20 to 25% of the intensity of the main peak. Presuming oxygen to be bound like in vitreous silica we can correct the spectrum of the silicon-carbon alloy with $x = 0.78$. Here we used the spectrum of quartz, measured under the same conditions as for the a- $\text{Si}_{1-x}\text{C}_x\text{:H}$ samples, which is very similar to that of vitreous silica. Figure 3 shows the Si K-emission band for $x = 0.78$ (curve A) and quartz (curve B). Curves A and B were scaled to equal height of the oxygen-related peak near 1818 eV and then subtracted. The difference spectrum (curve C) represents the carbon-rich sample of figure 2.

With increasing carbon content the Si K-emission bands gradually change in shape, looking very similar to each other for all Si-rich samples. The peak position shifts to lower energy (table 1). Simultaneously, the onset of the high-energy edge as obtained by extrapolation of the linear part of the slope moves towards higher energies by about 0.8 eV ($x = 0$: 1838.5 eV; $x = 0.78$: 1839.3 eV). In addition, the intensity of the high-energy tail (1839 to 1841 eV) increases, particularly for samples with larger carbon content. Both effects reflect a larger tailing of valence band states with composition parameter x consistent with a change of slope of the absorption edge [1, 2].

More pronounced changes occur on the low-energy side of the peak. There is an appreciable increase of intensity between 1830 and 1835 eV which leads to an increase of the FWHM. The increase of the linewidth occurs in small steps of 0.6 eV for silicon-rich samples going from $x = 0$ to $x = 0.47$ (table 1). The same increase of the linewidth is observed for the much smaller interval from $x = 0.47$ to $x = 0.62$. For $x = 0.78$ the width decreases again.

In the range between 1824 and 1827 eV a new feature emerges as the carbon content rises. This feature becomes noticeable for $x = 0.37$ as a weak but distinct bump, increasing its intensity at $x = 0.47$ somewhat and developing into a clearly resolved peak for $x = 0.62$. As indicated by vertical bars the position of this feature moves with increasing x to higher photon energy. It originates from Si-C bonds as will be discussed later. With further increase in x this feature is altered again, being broadened to a shoulder for $x = 0.78$.

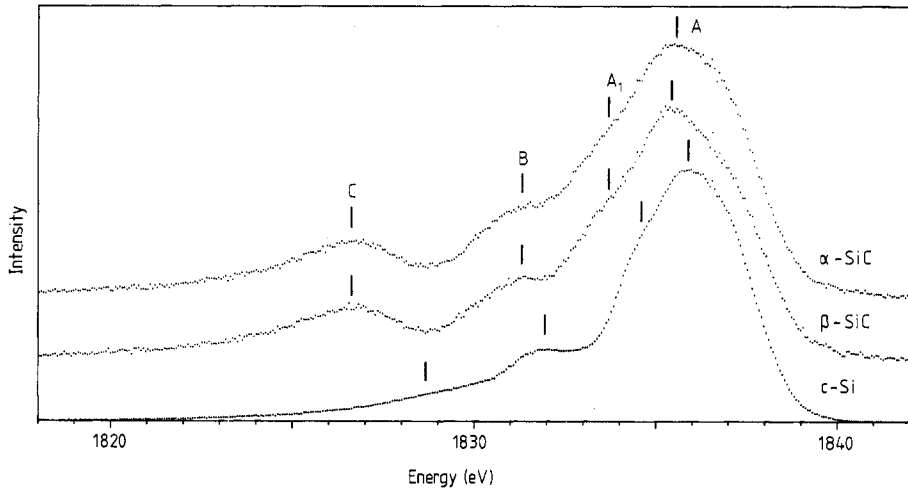


Figure 4. Si K-emission bands of crystalline silicon and hexagonal (α) and cubic (β) silicon carbide.

The Si K-emission band of the film with $x = 0.78$ differs also in its high-energy part from that of a film with $x = 0.62$. The FWHM is reduced to about 4.7 eV, the same width as found for α -SiC, and a shoulder near 1831 eV has developed similar to that observed in crystalline SiC (figure 4). On the whole, the top part (above 1830 eV) of the spectrum for $x = 0.78$ resembles more closely that of SiC than any other spectrum of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films while its low-energy part is smeared out, so the minimum found in the crystal near 1828 eV (figure 4) is not observed in the film.

3.3. Si K-emission bands of c-SiC

For comparison we will now consider the Si K-emission bands of α - and β -SiC which differ only in details (figure 4). Since the arrangement of nearest neighbours is identical for both structures (wurtzite for α -SiC and zincblende for β -SiC) the differences in the local partial DOS are caused by the different arrangement of next-nearest neighbours. Both the spectra of α - and β -SiC and of c-Si exhibit the same features, denoted by A, A_1 , B and C, which reflect sp^3 bonding. All parts of the spectra are broader in c-SiC than in c-Si and consequently the total width is larger. The FWHM is 3.75 eV in c-Si and 4.8 eV in c-SiC. The high-energy edge of the spectra agrees very well with respect to slope and position.

The basic properties of the spectra of the crystals are found also in the alloy films (figure 2): the bands become broader with increasing x and extend further down to low energies. Quantitatively, however, there are remarkable differences. A film of composition $x = 0.47$ should correspond to c-SiC, considering the carbon content. The low-energy peak, feature C, however, is much less developed in the film, its intensity reaching only 6% of that of the main peak instead of 20% as in the crystal. The emission band for $x = 0.62$ compares much better to that of c-SiC; here the low-energy peak reaches 17% of the intensity of the main peak, comparable to the relationship observed in the crystal. For $x = 0.78$ the intensity of C is lower again and the whole range is broadened.

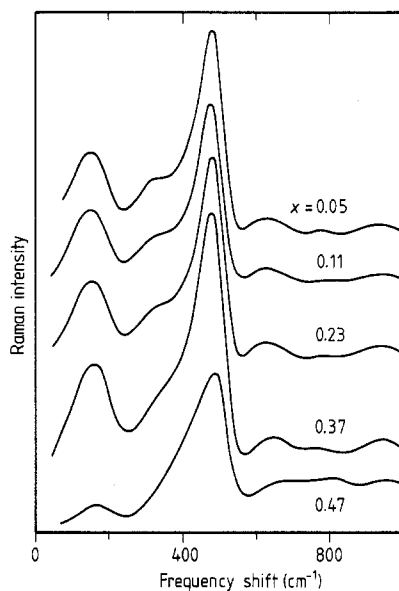


Figure 5. Raman spectra of $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ alloy films excited with an Ar laser (2.41 eV).

It should be mentioned that Solomon and co-workers [18] have also measured Si K-emission bands of $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ alloys. Their films are characterised not according to the composition parameter x but according to the silane/methane ratio in the gas discharge. From this ratio we estimate that their films have a composition with x between 0.2 and 0.6. On the whole their spectra develop in a similar way with rising carbon content as shown in figure 2. The FWHM they report, however, is always larger by some tenths of an eV and an increase by more than 2 eV when going from a methane concentration of 85% to 95% seems to be too large.

3.4. Raman spectra

Figure 5 shows Raman spectra for silicon-rich samples. These films were identical to those used for x-ray emission spectra except for the deposition on vitreous silica. Raman spectra for $x = 0.05$ are not distinguished from that of a-Si:H . The main feature, the peak at 478 cm^{-1} , remains stable in its position up to $x = 0.47$. This peak corresponds to a stretch mode of Si-Si bonds moved by about 43 cm^{-1} to lower energy as compared to that in the crystal. The shift reflects the weaker bonds in amorphous films. It is surprising that this peak shows no shift at all up to a considerable concentration of carbon. Because of the broadening on the low-energy side some details disappear with rising carbon content. Strong broadening together with a strong decrease of the low-energy peak around 150 cm^{-1} is observed for $x = 0.47$ pointing to the onset of large changes in the local environment of Si-Si bonds. For $x = 0.62$ and higher carbon content the dominant peak at 478 cm^{-1} has disappeared completely indicating a vanishing number of Si-Si bonds in the films. This striking change of the spectrum occurs in a narrow range starting near $x = 0.47$, the same range as that where the Si K-emission bands alter strongly showing new features and where the Si-related peak of the imaginary part ϵ_2 of the dielectric function disappears [1, 2].

Features characteristic for Si–C bonds and anticipated near 800 cm^{-1} have not been found in the samples studied here. The weak structures observed in this region correspond to modes related to Si–H bonds. Samples with $x > 0.47$ show when excited with an Ar laser considerable luminescence in the region of interest, obscuring any Raman intensity. Measurements with low-energy excitation may yield further information.

4. Discussion

The Si K-emission bands of the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloy films represent the p DOS with respect to the Si atoms, slightly modified by a matrix element. The spectra (figure 2) exhibit a gradual change of the steepness of the high-energy edge, the peak position, the FWHM and a new feature emerging near 1825 eV for higher carbon concentration, changes that are expected on the basis of the differences between c-Si and c-SiC (figure 4). A quantitative analysis, however, indicates that these changes cannot be interpreted as being due to gradual replacement of silicon atoms by carbon in a tetrahedrally coordinated network according to the composition parameter x .

Amorphous silicon can be considered as a tetrahedral network with distortions of bond length, bond angle and dihedral angle, with other than six-membered rings, with voids and dangling bonds [19]. In $a\text{-Si:H}$ hydrogen saturates dangling bonds and reduces strain [6, 20, 21]. We assume that the recession by 0.2–0.3 eV in the top part of the spectrum of $a\text{-Si:H}$ in comparison with the spectrum of $a\text{-Si}$ is caused by a reduction of such distortions. UPS spectra [22] show at binding energies of 6 and 11 eV features that are assigned to Si–H bonds. No such particular feature appears in the Si K-emission bands of $a\text{-Si:H}$ presented here, which indicates that the Si–H bonding states have predominantly s character while the Si 3p contribution is small.

The increase of carbon up to $x = 0.37$ is accompanied by a strong increase of hydrogen concentration. Nevertheless, this causes only minor alterations in the spectrum, and below 1832 eV, the region where features related to Si–C bonds should show up, the spectra for $x = 0$ and $x = 0.23$ are identical. Obviously the number of Si–C bonds is very small which supports the conjecture that most of the carbon atoms are not incorporated into a tetrahedral network but are bonded to hydrogen as CH_3 and CH_2 [1, 3]. As the carbon content increases further, the feature near 1825 eV which is related to C 2s states emerges, but even for $x = 0.47$ it is still very weak. Simultaneously the peak of the spectrum has shifted by 0.6 eV to lower energy and the FWHM has increased to 4.50 eV ($x = 0$: 3.95 eV; $x = 0.23$: 4.05 eV). From the small increase of the emission in the region around 1825 eV and from the shift and broadening of the peak we estimate that only about 10% at $x = 0.37$ and 20% at $x = 0.47$ of the bonds of Si in the alloys are Si–C bonds—values much less than anticipated from their composition.

At carbon concentrations of $x = 0.62$ a considerable change of the spectrum has occurred. The Si K-emission spectrum of these films now closely resembles that of c-SiC (figure 4). The low-energy feature C corresponds to the p DOS of the lowest of the valence bands and is characteristic of Si–C bonding. Its appearance in the spectra of the alloys is accompanied with a strong increase of the width of the peak, similar to that in the spectra of the crystals going from Si to SiC. Because of the confinement of Si 1s states, Si K-emission bands act as a local probe and reflect the bond behaviour in the close vicinity of the silicon atoms. The enormous change of the spectrum between $x = 0.47$ and $x = 0.62$ thus reveals large changes in the short-range order. The close resemblance of the spectrum for $x = 0.62$ to the spectrum of c-SiC on the other hand indicates that

around Si atoms we still have a tetrahedrally coordinated lattice with a majority of Si–C bonds.

In the most carbon-rich sample ($x = 0.78$) where the number of carbon atoms by far exceeds that of silicon, it is thought that Si–C bonds prevail in the Si K-emission spectrum. The peak does indeed look very similar to that of c-SiC, even showing some of the fine structure on its low-energy side near 1834 and 1831 eV. The FWHM has decreased again as compared with the spectrum for $x = 0.62$ which may point to a more fully relaxed local structure around Si atoms, which is probably very similar to that of c-SiC. This conjecture seems to disagree with the behaviour of feature C near 1825 eV, which broadens on going from $x = 0.62$ to $x = 0.78$. This part of the spectrum is related to C 2s states which, since they have some p character with respect to Si atoms, are observable in the Si K-emission band. In carbon-rich samples SiC_x clusters are embedded in a carbon-based matrix still containing a large amount of C–H bonds. The different evolution of feature C and the main peak of the Si K-emission band with increasing carbon content points to some influence of this matrix on the C 2s–Si 3s, 3p interactions. Further information is expected from the study of the Si L-emission bands (at photon energies near 90 eV), reflecting the s-like DOS at silicon atoms and, in particular, from C K-emission bands (near 270–280 eV) which probe the DOS at carbon atoms. Such studies are in progress.

In conclusion we find that the valence band structure of a- $\text{Si}_{1-x}\text{C}_x\text{:H}$ alloys changes only moderately for silicon-rich samples and remains very similar to that of a-Si:H for compositions up to $x = 0.47$. At this composition a change of the local structure around Si atoms, which are still predominantly bound by Si–Si bonds, sets in. This alteration of the bonding configuration of Si atoms is completed in films with a composition $x = 0.62$. This is in agreement with the optical data reported by Sotiropoulos and co-workers [1, 2], who observed sudden changes of the absorption edge, of the reflectivity and of the ϵ_2 -spectra in the same range of composition, which they interpreted as being due to the breakdown of a Si-based network taking place when the density of silicon atoms becomes too small. The stability of the Si-based lattice is also evident from the Raman data (figure 5). In particular, the peak corresponding to the stretch mode of Si–Si bonds remains very stable up to $x = 0.47$. The position of this peak is related to the bond strength and should therefore be sensitive to a variation in bond length of Si–Si atoms. Apparently this is not the case as long as Si–Si bonds determine the structure of the films. If these bonds are diluted too much, which they evidently are at compositions close to $x = 0.5$, the structure of the films changes and Si–C bonds determine the structure of the films. The number of Si–Si bonds decreases so rapidly that they are no longer discernible in the Raman spectrum of a film with $x = 0.62$.

The preference for a Si-based network in a- $\text{Si}_{1-x}\text{C}_x\text{:H}$ films is certainly related to the larger stability of methane as compared to silane, which for the discharge parameters chosen leads to incorporation of carbon mainly as CH_2 and CH_3 groups. The smooth and gradual change of the optical properties reported by Mui and co-workers [3, 4] for ethylene-based films contradicts the assertion of such a preference for a Si-based network. The possibility cannot be excluded that this discrepancy may arise from different preparation conditions, although such different kinetics in the growth of the films is hard to understand in view of the stability of ethylene.

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