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# Electronic structure of carbon-rich a-Si<sub>1-x</sub>C<sub>x</sub>H<sub>y</sub> alloys: the role of hydrogen and graphitic carbon

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**Abstract.** We calculated the electronic structure of carbon-rich a-Si<sub>1-x</sub>C<sub>x</sub>H<sub>y</sub>, an alloy for which there is conflicting experimental evidence for the degree of disorder and the fraction of graphitic carbon atoms present. Our calculation takes into account valence disorder due to carbon and hydrogen as well as short-range order effects. We deduce that, if the alloy is heavily hydrogenated, then Si–Si bonds exist in considerable amount up to  $x = 0.75$  at least. Furthermore the fraction of graphitic carbon atoms increases slowly up to the value of  $x$  at which a maximum in the band gap occurs and then it increases rapidly as some experiments seem to confirm. Our calculated band gap as a function of  $x$  is in reasonable agreement with experiment and our peaks in the density of states (DOS) correlate well with the peaks of the photoemission spectra whose orbital character we can deduce. We note that our conclusion on the presence of Si–Si bonds is independent of our method of calculating the DOS and derives from our matching of atoms to the corresponding bonds. Finally estimates of the fraction of graphitic atoms at each  $x$  are made.

## 1. Introduction

The a-Si<sub>1-x</sub>C<sub>x</sub>H<sub>y</sub> system has been investigated intensely in the last 15 years (see [1,2] and references therein). The  $x < 0.4$  region of compositions where the band gap changes linearly with  $x$  is well understood now. A recent calculation by one of us [3] has explained most of the relevant experimental data for this range. By comparison, several problems regarding the structure of this alloy in the  $x \geq 0.5$  region of compositions remain. These are the following.

(1) *The type of short-range order (SRO) present.* The EXAFS experiments of Pascarelli *et al* [4], the XRD results of Meneghini *et al* [5] and the EELS experiments of Kaloyeros *et al* [6] point to chemical order whereas the Raman spectra of Gorman and Solin [7] and the XRD study of Tejada *et al* [8] show a considerable number of homopolar bonds.

(2) *The ratio of sp<sup>2</sup> to sp<sup>3</sup> carbon atoms.* Katayama *et al* [9] found that this ratio is important only in carbon-rich alloys and increased rapidly after  $x > 0.5$  whereas NMR measurement [10] showed the presence of sp<sup>2</sup>-bonded carbon atoms at much smaller  $x$ .

(3) *The factors affecting the appearance of a maximum in the  $E_g(x)$  curve* (although a qualitative explanation of its shape has been given [1]). The maximum appears usually between  $x = 0.6$  and  $x = 0.7$  [11, 12] but it has been measured to be as low as  $x = 0.4$  [13]. This divergence of experiment and opinion can be partly explained by the fact that, as is now accepted, the structure of these alloys depends critically on the method of preparation [1, 2] and the amount of hydrogen present. The latter is of particular significance since it

increases considerably the fraction of tetravalent carbon atoms by the formation of  $sp^3$  C–H bonds [14]. This has a profound effect on the band gap. Robertson [1] has attributed the appearance of the maximum in the  $E_g(x)$  curve to the substantial onset of  $C_\pi$  states at  $x \approx 0.6$ – $0.7$ . If hydrogen can control the fraction of  $sp^2$  C, then it can indirectly influence the band gap. As we shall see later, it does so in another way also, by promoting Si–Si bonds.

So far no calculation has taken both the above two factors, namely  $sp^2$  carbon and hydrogen, into account in a single calculation. Previous calculations, although with differing results, have contributed to a better understanding of the experimental results. The *ab-initio* molecular dynamics of Finocchi *et al* [15] for the  $Si_{1-x}C_x$  system predict a considerable number (40%) of homopolar C–C bonds, and 10–15% of  $sp^2$  carbon. They showed also why, despite this disorder, the Si–C bonds are overemphasized in the measured scattered intensities because of their higher atomic factors. The Monte Carlo simulations of Kelires [16], on the other hand, predict, for the same system, a lower number of C–C bonds and a much higher ratio of  $sp^2$  C (40–50%). He stated that this ratio will be smaller in hydrogenated samples. Robertson [1] in his electronic structure calculations took into the account the presence of Si–H and C–H bonds but his calculations [1] were mostly relevant to the  $x < 0.5$  case since he used a simplified virtual-crystal approximation. However, qualitative predictions of the degree of disorder for  $x > 0.5$  were made namely that a medium degree of disorder exists. A previous density-of-states (DOS) calculation by one of us [17] while taking into account the presence of  $sp^2$  carbon was mainly directed at lightly hydrogenated samples. The same holds true for the DOS calculation of Kelires and Denteneer [18] which was of qualitative character because of the serious underestimation of the band gap at all  $x$ .

In this paper we aim at resolving the above issues by performing calculations of the electronic structure of  $a-Si_{1-x}C_xH_y$  alloys which are sensitive the SRO of the atoms and which take full account of the valence disorder introduced by  $sp^2$  carbon and hydrogen. Such a method is that of Gomez-Santos and Verges [19]. It is worth noting here that the question of the existence of homoatomic bonds can be answered without having to resort to any calculations of the DOS of the material. In particular we show that, if the alloy is heavily hydrogenated (50%), then Si–Si bonds must necessarily be present although the converse is not necessarily true. From our calculated local DOS we are also able to identify the origin of all the peaks of the photoemission spectra of Katayama *et al* [20]. Furthermore we show that for the  $E_g(x)$  curve to have a maximum of  $x \approx 0.65$  a sudden increase in the ratio of  $sp^2$  C must occur at the same  $x$ , as has been seen experimentally [9] and has been inferred also by the cluster calculation of Zdetsis [21].

Finally we tentatively argue that  $a-Si_{1-x}C_xH_y$  is not a typical amorphous semiconductor for  $x > 0.5$ . The DOS of the tail states does not decrease rapidly (say exponentially) inside the gap as indeed has been seen in the photoemission spectra of Fang and Ley [22] and De Seta *et al* [23] and furthermore it is not clear that such a tail is composed of localized states only. Similar arguments for  $a-(C-H)$  have been advanced by Dasgupta *et al* [24] based on their optical measurements. In the next section we briefly but critically describe the method that we use to determine its suitability for problems such as those mentioned above. The choice of our tight-binding (TB) parameters is also given.

## 2. Method

As mentioned in the introduction we have used the method of Gomez-Santos and Verges [19] to obtain the configurationally averaged DOS. According to this method the real lattice is

simulated by a Bethe (tree) lattice which has the appropriate coordination at each point, i.e. the geometry of the particular atom occupying the particular lattice site. This conceptual (or geometric) simplification, which has proved very efficient for amorphous semiconductors, leads to the following algebraic simplification.

The local DOS  $n_{l,i}(E)$  which is due to a particular orbital  $l$  of an atom of type  $i$  can always be written as

$$\begin{aligned} n_{l,i}(E) &= \lim_{\delta \rightarrow 0} \left( -\frac{1}{\pi} \langle l, i | (E + i\delta - H)^{-1} | l, i \rangle \right) \\ &= \lim_{\delta \rightarrow 0} \left( -\frac{1}{\pi} \langle l, i | (E + i\delta - \epsilon_{l,i} - \Sigma_{l,i}(E))^{-1} | l, i \rangle \right) \end{aligned}$$

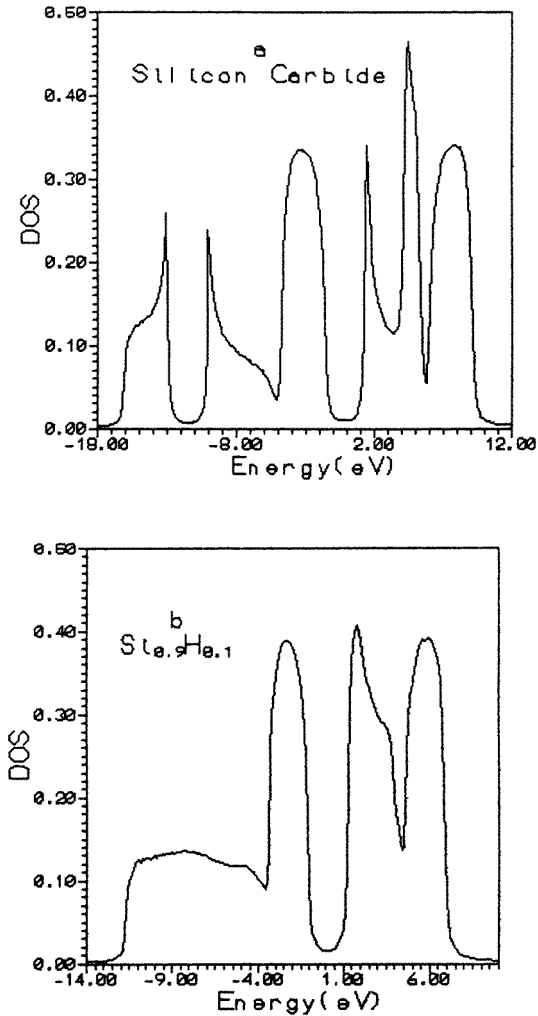
where  $\epsilon_{l,i}$  are the diagonal matrix elements of the Hamiltonian  $H$  and  $\Sigma_{l,i}(E)$  are the corresponding self-energies. The above-discussed geometric simplification allows one to obtain explicit equations linking the various  $\Sigma_{l,i}$  between them. This has the advantage that one does not have to do numerical calculations on a cluster of atoms and the only numerical work involved is in solving the equations for  $\Sigma_{l,i}$ . We have obtained two self-energies for C: one for the trivalent and one for tetravalent C.

The procedure for obtaining these equations is well known [25,26] so that nothing further about this needs to be stated.

The method has worked successfully for many amorphous semiconductors [25,27] but there is no reason to believe that this will be so in every case. A prerequisite is that the DOS is determined essentially by the SRO of the material in question. Figure 1(a) gives the DOS of c-SiC. The TB parameters are essentially those given by Robertson [1]. Only  $pp\sigma$  has been changed to 3.94 eV. It can be seen that the characteristic three-peak structure of zincblende semiconductors is well reproduced and the band gap is fixed at 2.5 eV by the small change in  $pp\sigma$ . The important thing to notice is that the small tail inside the gap is only an artefact of having to do the calculations on the computer with a finite  $\delta$ . Obviously it can be made successively as small as possible or more practically a very small  $\delta$  can be chosen and a linear extrapolation of the bands very near the edges can be used to obtain the band gap  $E_g$ .

Real amorphous semiconductors have tails of course, which are composed of localized states and are exponentially decreasing into the gap. The band gap  $E_g$ , as defined in the paragraph above, is to be compared with the Tauc gap  $E_T$ . This is because cutting off the tails amounts to making the bands parabolic as Tauc assumed them to be. The more commonly measured optical gap  $E_{04}$  is normally greater than  $E_T$  by 0.1–0.15 eV since some contribution from the Urbach tail to the absorption process always occurs. These latter comments although widely known have particular relevance to our problem, as will be seen below.

Figure 1(b) gives the DOS of Si<sub>0.9</sub>H<sub>0.1</sub>. Again by an appropriate small change in  $pp\sigma$  (Si–Si) to 2.92 eV the band gap has been fixed at 1.8 eV, equal to the value of  $E_T$  for a-Si: H with 10% hydrogen. Note that the DOS is not composed of a three-peak structure but has a simpler form which, however, resembles the experimental x-ray photoelectron spectrum of Si [28]. The Bethe lattice seems to simulate well this change in shape, from the spectrum of c-Si to that of a-Si, which is due to the loss of long-range order (LRO). This difference between the DOSs of the amorphous and crystalline phases occurs only if the semiconductor contains homonuclear bonds. Figure 1(c) gives the DOS of amorphous tetracoordinated (diamond) carbon, with a  $pp\sigma$  of 4.6 eV. The same comments as for a-Si are applicable here.



**Figure 1.** DOS of 'end-point' semiconductors: (a) SiC; (b)  $\text{Si}_{0.9}\text{H}_{0.1}$ ; (c) diamond-like carbon; (d) graphitic carbon.

We now consider our calculated DOS of amorphous tricoordinated (graphitic) carbon (figure 1(d)). As expected (from the existence of homonuclear bonds) the shape of the curve is much simpler than the x-ray photoelectron spectrum of crystalline graphite but the structures of its peaks are in very good agreement with the a-C x-ray photoelectron spectrum obtained by Katayama *et al* [20] (see figure 5 later) who used samples which were mostly  $\text{sp}^2$  bonded. Furthermore an almost constant tail of states connects the valence and conduction bands. This tail, although overestimated near the middle, is in agreement with the total yield photoemission spectra obtained by De Seta *et al* [23]. In these spectra no abrupt decrease in the signal near the photothreshold is recorded but the signal decreases slowly for another 2 eV below this. A similar behaviour is observed in the optical data of Dasgupta *et al* [24]. The origin of these states has been attributed to fivefold and sevenfold carbon rings [1]. An almost zero DOS at  $E_F$  appears only if sixfold rings are exclusively present.

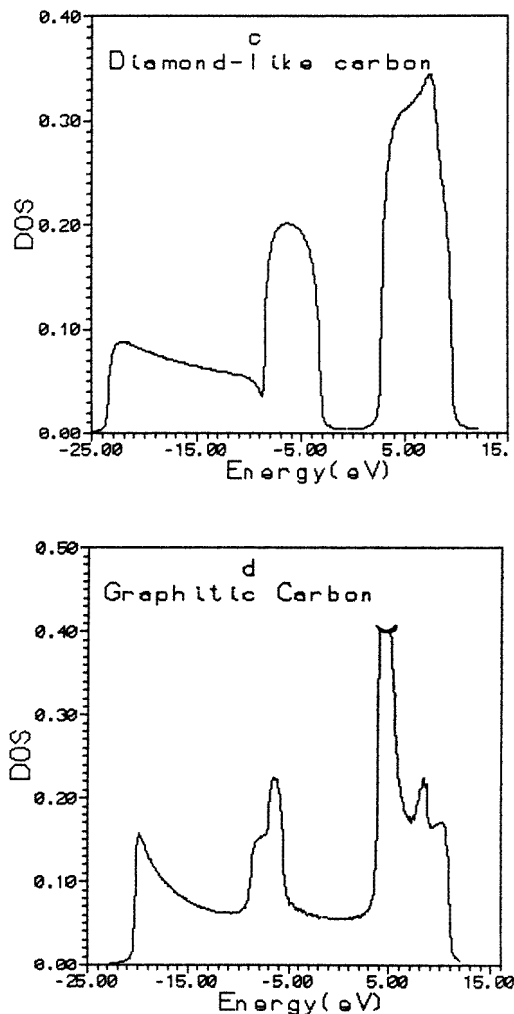


Figure 1. (Continued)

As a result of the above, any DOS of the alloy  $\text{Si}_{1-x}\text{C}_x\text{H}_y$  will contain a small tail in the gap (see our results in figure 3 later) which has nothing to do with the small imaginary  $\delta$  in the Green function. The question then arises of how to define such a gap. One could calculate  $a(\omega)$ , the absorption coefficient, and then determine  $E_{04}$ . The necessary approximations, however, in evaluating both  $\langle i/p/j \rangle$  and  $\langle i/G/j \rangle$ ,  $i \neq j$ , make this an inaccurate procedure. We have opted for the more physically appealing method of linear extrapolation near the band edges which effectively cuts off the band tails and is more in line with the notion of a Tauc gap, i.e. effectively evaluating the energy difference between two approximately parabolic bands of extended states with their tails of localized states cut off. A similar procedure has been adopted by Dasgupta *et al* [24] in their analysis of the optical data for a-C:H. On the other hand, one should observe that it is not at all obvious that this tail contains localized states only. We shall discuss this in the next section. Here we only note that firstly our band gap  $E_g$  obtained thus is expected to be smaller than the

corresponding experimental  $E_{04}$  by 0.1–0.2 eV and secondly we have carefully avoided the  $x > 0.85$  region where medium-range order (MRO) will play a role because of probable clustering of  $sp^2$  carbon atoms.

### 3. Results

We rewrite the alloy  $Si_{1-x'}C_{x'}H_{y'}$ , in the more analytical form  $Si_xC_y^4C_z^3H_w$  where  $x + y + z + w = 1$ , and  $C^4$  and  $C^3$  denote the tetravalent and trivalent carbon atoms, respectively. The experimental data [10, 14] show that most hydrogen is bonded to  $C^4$  for  $x > 0.5$ . Then we need to consider only the bonds with probabilities  $P(\text{Si-Si}) = g$ ,  $P(\text{Si-C}^4) = k$ ,  $P(\text{C}^4\text{-C}^4) = l$ ,  $P(\text{C}^3\text{-C}^3) = n$ ,  $P(\text{C}^4\text{-C}^3) = m$  and  $P(\text{C}^4\text{-H}) = q$ . We have excluded the probability of  $\text{Si-C}^3$  bonds. By requiring that all atoms saturate all kinds of bond we get the following four equations:

$$2g + k = 4xc \quad (1)$$

$$k + 2l + m + q = 4yc \quad (2)$$

$$m + 2n = 3zc \quad (3)$$

$$q = wc \quad (4)$$

where  $c = 2(4x + 4y + 3z + 4w)^{-1}$  is a normalization constant. For the method of deriving such equations see [29].

This is a system of four equations and six unknowns so that two bond probabilities must be treated as SRO parameters so that the set of equations becomes solvable. We choose these to be  $g$  and  $n$ . Since all probabilities must remain positive, we get from (1)

$$g < 2xc \quad (5)$$

from (3)

$$n < 3zc/2 \quad (6)$$

and from (2) after some algebra

$$g + n > 1 - 4yc. \quad (7)$$

Now it is the consensus of most experimental groups that the hydrogen content saturates at 50% for  $x' > 0.4$ , so that at, say  $x' = 0.55$  one has that  $y' = 1$  and the stoichiometric indices become, with say 10% of carbon in trivalent form,  $x = 0.225$ ,  $y = 0.248$ ,  $z = 0.027$  and  $w = 0.5$ . With these values of  $x$ ,  $y$ ,  $z$  and  $w$  the above inequalities (5)–(7) become

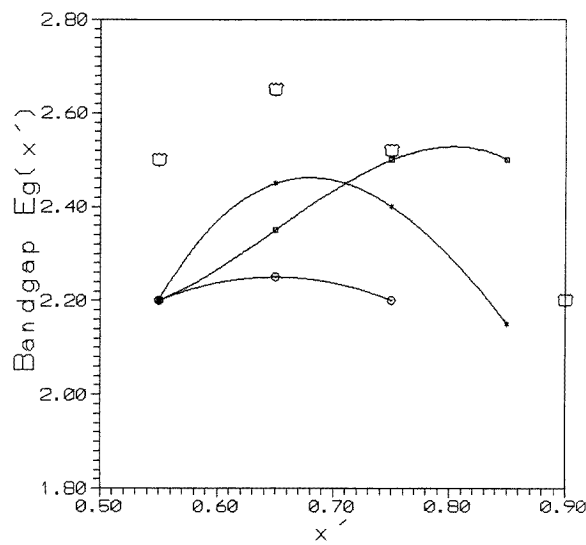
$$g < 0.364 \quad n < 0.033 \quad g + n > 0.199.$$

Obviously  $g = 0$  is not a solution of the above system and some Si–Si bonds must necessarily be present. In fact  $g$  must be at least 0.166 in this case. This is an example of a consistent pattern where a substantial but diminishing number of Si–Si bonds exists up to at least  $x' = 0.75$ . This result is obviously independent of our method of calculating the DOS and it could have been anticipated intuitively. Consider a hypothetical c-SiC source of Si and C atoms. Once the hydrogen atoms enter the system and form C–H bonds, the Si atoms, which were originally bonded to C, have no other alternative but to bond each other unless the C atoms are in substantial excess and can take up the hydrogen without breaking Si–C bonds. Our analysis gives exact numerical bounds for the various proportions of bonds consistent with the stoichiometric indices. Now the absence of hydrogen does not necessarily mean the absence of disorder. However, varying degrees of hydrogen content will promote varying degrees of disorder. Therefore the notion that hydrogen promotes

chemical order should be properly interpreted. Indeed it increases the proportion of C<sup>4</sup> atoms at the expense of C<sup>3</sup> atoms and in doing so it removes states from the gap but at the same time it promotes the formation of Si-Si bonds at least for  $x' < 0.75$ .

As noted in the introduction there is conflicting experimental evidence [9, 10] about the ratio  $\alpha(x')$  of carbon atoms in trivalent form. This quantity, apart from being a quantity of considerable physical importance in itself, is also a prerequisite to any calculation of the DOS of the alloy since it determines the stoichiometric indices  $y$  and  $z$ . In fact one needs  $x'$ ,  $y'$ ,  $\alpha$  and the SRO parameters  $p$  and  $n$  to determine the DOS completely since the self-energies  $\Sigma_{A,l}$  of an atom of type A depend on all the conditional probabilities  $p_{AB}$  that B is a neighbour of A, i.e. the inclusion of SRO has made the problem quite complex. We have found it possible, however, to determine at least semiquantitatively the variation in  $\alpha$  with  $x'$ .

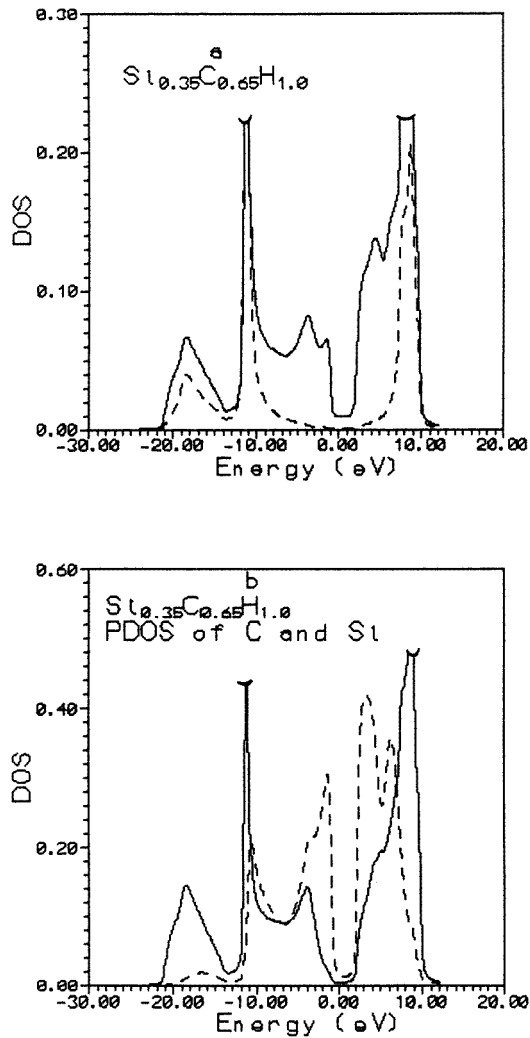
We have performed three sets of calculations of the band gap  $E_g$  as a function of  $x'$ , each set belonging to a different type of variation for  $\alpha(x')$ . In each case  $p, n$  were assigned values



**Figure 2.** Variation in the bandgap  $E_g$  as a function of the index  $x'$  for various configurations given by the fraction of  $sp^2$  C and the SRO parameters  $g$  and  $n$ . The irregular symbols not connected by a line denote experimental levels from reference [11].

Symbol	$x'$	$y'$	$\alpha$	$g$	$n$
□	0.55	1	0.10	0.18	0.02
□	0.65	1	0.20	0.14	0.04
□	0.75	1	0.30	0.10	0.07
□	0.85	0.8	0.40	0.06	0.12
○	0.55	1	0.10	0.20	0.03
○	0.65	1	0.30	0.18	0.09
○	0.75	1	0.50	0.16	0.21
*	0.55	1	0.10	0.18	0.02
*	0.65	1	0.15	0.14	0.03
*	0.75	1	0.35	0.10	0.08
*	0.85	0.8	0.55	0.06	0.23





**Figure 3.** (a) DOS of  $\text{Si}_{0.35}\text{C}_{0.65}\text{H}_1$  with  $\alpha = 0.15$  (—) and unweighted partial density of states (PDOS) of H (---), (b) PDOS (unweighted) of C (—) and Si (---).

approximately half-way along the range allowed by the inequalities (5)–(7). The results are shown in figure 2. In the first set,  $\alpha(x')$  changes linearly in steps of 0.1 starting from  $\alpha = 0.10$  at  $x' = 0.55$  (small variation), in the second it changes linearly in steps of 0.2 (large variation) and in the third  $\alpha(x')$  changes slowly in the beginning and then jumps between  $x' = 0.65$  and  $x' = 0.75$ , increasing quickly thereafter. In all cases the hydrogen content  $y'$  was the average of those determined experimentally in [30] and in [31]; see the figure caption for the values of all parameters. It can be seen that only this last type of variation produces a corresponding variation in  $E_g(x')$  which has a clear maximum between  $x' = 0.65$  and 0.75. The linear increase in  $\alpha(x')$  with small steps produces an almost monotonically increasing  $E_g(x')$ , and the increase with large steps produces an almost flat  $E_g(x')$ .

We have made sure by repeated tests that this form of  $E_g(x')$  is the result of the corresponding variation in  $\alpha(x')$  and is not the outcome of some strange combination of values

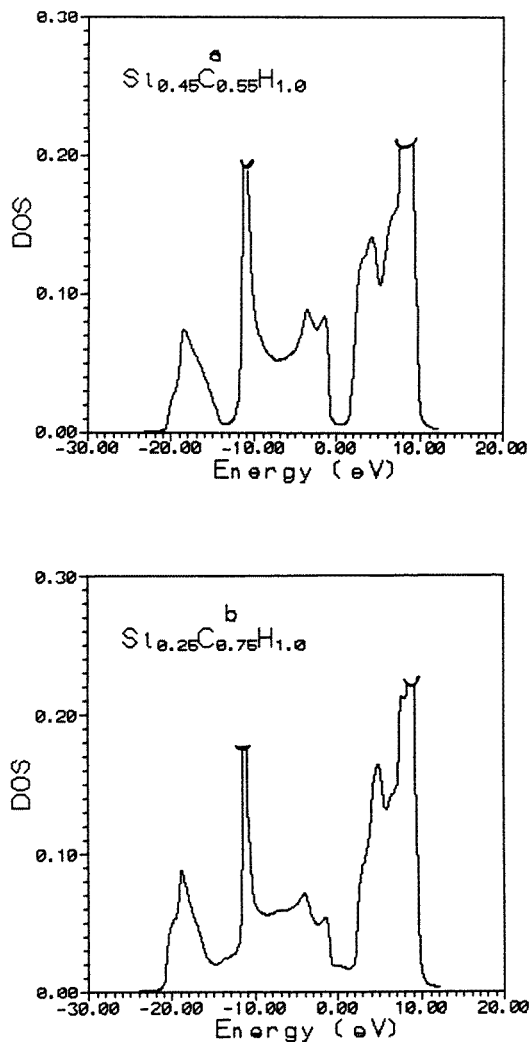
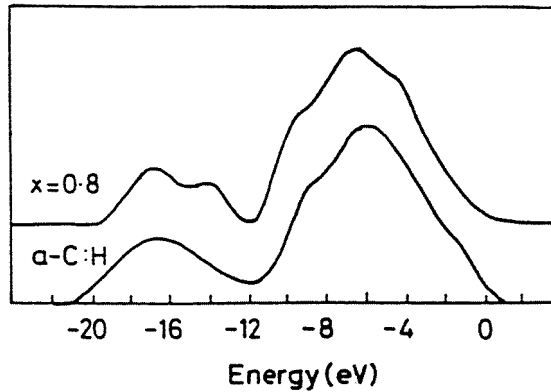


Figure 4. (a) DOS of  $\text{Si}_{0.45}\text{C}_{0.55}\text{H}_1$  with  $\alpha = 0.10$ , (b) DOS of  $\text{Si}_{0.25}\text{C}_{0.75}\text{H}_1$  with  $\alpha = 0.35$ .

in  $p$  and  $n$ . Although changes in these latter parameters may affect the band gap slightly, a clear maximum appears only if  $\alpha(x')$  suddenly increases immediately after the maximum. As noted earlier, evidence for this may be found in the work of Katayama *et al* [9], where the width of the plasmon line shows a sudden increase between  $x' = 0.4$  and  $0.6$  due to the appearance of damping states in the gap. Zdetsis [21] also came to the same conclusion theoretically from his cluster calculations. He observed a lattice transformation from diamond like to graphitic at  $x' \approx 0.5$ . We note that the appearance of the maximum at  $x' = 0.4$  in [13], as opposed to  $x' = 0.6$ – $0.7$  in all the other experimental data, may be due to a smaller hydrogen content. As expected, our calculated values of  $E_g$  are smaller than the experimental values by  $0.15$ – $0.2$  eV. This is quite satisfactory considering that this value represents the difference between the Tauc gap  $E_T$  and  $E_{0.4}$  in most semiconductors. Our values of  $P(\text{Si-Si})$  as a function of  $x'$  suggest that in the alloy a medium degree of disorder exists.



**Figure 5.** Experimental photoemission spectra of carbon-rich a-SiC:H obtained by Katayama [20], reproduced from Robertson [1].

Our calculated DOSs for the values of the parameters for which a maximum in  $E_g(x')$  appears are shown in figures 3 and 4. In figure 3(a) we present the DOS at  $x' = 0.65$  together with the PDOS of hydrogen. The orbital content of each peak can be deduced from this PDOS and the PDOSs of Si and C<sub>4</sub> shown in figure 3(b). The peaks at  $-19$  and  $-11$  eV derive from C–H bonds (the lower is s like and the upper p like), the peak at  $-4$  eV is mainly due to carbon, and the peak at  $-2$  eV is due to silicon. On comparing the XPS data of Katayama *et al* [20] (figure 5) we see that there is a fair correspondence between our peaks and theirs. However, certain peaks in our DOS are seen only as shoulders in their spectra. Furthermore the peak at  $-14$  eV in their spectra is seen as a shoulder at approximately  $-15$  eV in our calculations. This is because the states in the spectra are weighted by the appropriate scattering cross section of each state; for example the C–H states have much lower cross sections than all the rest. There is general agreement in the literature about the assignment of these peaks. A small disagreement about the peak at  $-14$  eV [1] can be resolved by looking at our PDOSs. This peak is of mixed Si and C<sub>4</sub> character and therefore should be attributed to Si–C bonds. Note that, although the PDOS of Si has a peak at  $-15$  eV, the PDOS of C<sub>4</sub> does not but it has a greater contribution at this energy. This is because the original peak of the PDOS of C in the stoichiometric SiC compound is masked by the  $-19$  eV peak owing to C–H bonds.

Figures 4(a) and 4(b) show the calculated DOSs for  $x' = 0.55$  and  $x' = 0.75$ , respectively. The figures are qualitatively the same. Two systematic differences occur in going from  $x' = 0.55$  through  $x' = 0.65$  to  $x' = 0.75$ . First the shoulder of the lower valence band moves from  $-15$  to  $-19$  eV. This is due to the increased carbon content and the explanation should be evident in view of the discussion in the previous paragraph. Most importantly, however, one can see that the height of the tail in the gap increases monotonically (taking figure 3(a) also into account). These states, as already discussed, come from the trivalent carbon atoms. The question naturally arises of whether these states, namely the tail states, are localized states in the traditional sense of the word. The following last argument is qualitative and tentative and a more advanced theory is needed to answer this question.

At  $x' \approx 0.5$  the sp<sup>2</sup>-bonded C atoms will be scattered and isolated in the lattice and therefore their states are bound to be localized. As  $x'$  is increased beyond  $x' = 0.65$  and

their number increases substantially, the percolation threshold (the critical concentration at which an infinite cluster forms) will eventually be reached and these states will certainly be extended. Hybridization with sp<sup>3</sup> C, however, will make these states extended before the percolation limit is reached. Even the calculation of the latter limit is more difficult than usual. The lattice is not static; it changes shape with  $x'$ . These problems are beyond the scope of this paper.

#### 4. Conclusions

We have shown that the a-Si<sub>1-x</sub>C<sub>x</sub>H<sub>y</sub> alloy has necessarily a considerable number of Si-Si bonds if the hydrogen content is as high as most experimentalists have determined i.e. around 50%. This conclusion is independent of our method of calculating the DOS and rests entirely on the fact that C bonds preferentially to H. By calculating the band gap and comparing it with the experimental value we have shown that for the  $E_g(x)$  curve to have a maximum at  $x \approx 0.65$  the number of C<sub>3</sub> atoms must increase abruptly immediately beyond this  $x$ . Also a medium degree of homopolar bonds exists. Our calculated band gaps are in reasonable agreement with experiment. Finally our calculated DOSs compare well with the x-ray photoelectron spectra and we have identified the origin of all the peaks in the latter.

#### References

- [1] Robertson J 1992 *Phil. Mag.* B **66** 615
- [2] Evangelisti F 1993 *J. Non-Cryst. Solids* **164-6** 1009
- [3] Xanthakis J P 1994 *J. Phys.: Condens. Matter* **6** 10 457
- [4] Pascarelli S, Boscherini F, Mobilio S and Evangelisti F 1992 *Phys. Rev. B* **45** 1650
- [5] Meneghini C, Pascarelli S, Boscherini F, Mobilio S and Evangelisti F 1991 *J. Non-Cryst. Solids* **137-8** 75
- [6] Kaloyeros A E, Rizk R B and Woohouse J B 1988 *Phys. Rev. B* **38** 13 099
- [7] Gorman M and Solin S A 1974 *Solid State Commun.* **15** 761
- [8] Tejada J, Shevchik N J and Cardona M 1974 *Amorphous and Liquid Semiconductors* ed J Stuke (London: Taylor and Francis) p 557
- [9] Katayama Y, Shimada T and Usami K 1981 *Phys. Rev. Lett.* **46** 1146
- [10] Petrich M A, Gleason K K and Reimer J A 1987 *Phys. Rev. B* **36** 9722
- [11] Sussman R S and Ogden R 1981 *Phil. Mag.* B **44** 137
- [12] Sotiropoulos J and Weiser G 1987 *J. Non-Cryst. Solids* **97** 1087
- [13] Shimada T, Katayama Y and Komatsubara K F 1979 *J. Appl. Phys.* **50** 5530
- [14] Baker S H, Spear W E and Gibson R A G 1990 *Phil. Mag.* B **62** 213
- [15] Finocchi F, Galli G, Parrinelo M and Bertoni C M 1992 *Phys. Rev. Lett.* **20** 3044
- [16] Kelires P C 1991 *Europhys. Lett.* **14** 43
- [17] Xanthakis J P 1993 *J. Non-Cryst. Solids* **164-6** 1019
- [18] Kelires P C and Denteneer P J H 1993 *Solid State Commun.* **87** 851
- [19] Gomez-Santos G and Verges J A 1987 *J. Phys. C: Solid State Phys.* **20** 5001
- [20] Katayama Y, Shimada T, Uda T and Kobayashi K L I 1983 *J. Non-Cryst. Solids* **59-60** 561
- [21] Zdetsis A D 1989 *J. Non-Cryst. Solids* **114** 513
- [22] Fang R C and Ley L 1989 *Phys. Rev. B* **40** 3818
- [23] De Seta M, Fiorini P, Coppola F and Evangelisti F 1991 *J. Non-Cryst. Solids* **137-8** 867
- [24] Dasgupta D, Demichelis F, Pirri C F and Tagliaferro A 1991 *Phys. Rev. B* **43** 2131
- [25] Martin-Moreno L, Martinez E, Verges J A and Yndurain F 1987 *Phys. Rev. B* **35** 9683
- [26] Xanthakis J P 1992 *J. Phys.: Condens. Matter* **4** 8573
- [27] Xanthakis J P, Katsoulakos P and Georgiakos D 1993 *J. Phys.: Condens. Matter* **5** 8677
- [28] Kärcher R, Ley L and Johnson R L 1984 *Phys. Rev. B* **30** 1896
- [29] Kittler R C and Falicov L M 1976 *J. Phys. C: Solid State Phys.* **9** 4259
- [30] Kuhman D, Grammatica S and Jansen J 1989 *Thin Solid Films* **177** 253
- [31] Beyer W 1987 *J. Non-Cryst. Solids* **97** 1023