Electronic structure of Si-rich a-Si$_{1-x}$C$_x$H$_y$ alloys

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Abstract. We have calculated the electronic structure of amorphous hydrogenated Si-rich
Si$_{1-x}$C$_x$H$_y$ alloys paying particular attention to methylated Si, i.e. alloys produced at low
deposition power with CH$_3$ configurations only and no C–C bonds. The configurational
averaging method we use produces densities of states (DOS) which are not only a function
of the compositional indices but also of the short-range order (SRO) parameters. By varying the
DOS with respect to these parameters we are led to deduce the origin of all the experimental XPS
peaks including the one at −14 eV which is assigned to Si(s) and C(s) orbitals in Si–C bonds.
The calculated band gaps of the alloys produced at high deposition power are in good agreement
with experiment and tentatively point to a small to medium degree of disorder. On the other
hand the calculated band gaps of methylated Si is in remarkable agreement for $x < 0.25$ when
the CH$_3$ configuration is known to prevail but deviates considerably from the very high recently
published experimental band gaps near $x \sim 0.4$ suggesting that the model of methylated Si may
require modification for these values of x.

1. Introduction

Novel experiments by Solomon and co-workers [1,2] have revealed a new phase of
aSi$_{1-x}$C$_x$H$_y$ which they have called 'methylated amorphous silicon'. This is produced
when, during RF plasma deposition, the deposition power density is low enough so that the
CH$_4$ gas—unlike the SiH$_4$—is not decomposed and therefore carbon is not deposited directly
but by a chemical reaction of methane with the dissociated radicals of silane. Therefore
in the final product each C is expected to be surrounded by three H atoms and one Si in
tetrahedral coordination. Experimental evidence for such a model exists in the measured
atomic ratio of H to C which increases linearly with x with a slope of three up to $x = 0.20$.
For $x > 0.20$ the number of H nearest neighbours (NN) of C starts to decrease while the H
content seems to saturate at $y = 0.85$ near $x = 0.30$. At the other end of the composition
range ($x = 0$), 10% of H is added to the system to give the optimised a-Si:H material.

The particular structure of this material has a pronounced effect on its optical properties.
The measured band gap (E_{04}) is substantially higher than any other produced so far and
varies almost linearly between 1.9 eV at $x = 0$ and 2.45 at $x = 0.20$. Very recent results by
the same group [3] for higher carbon concentrations have produced record values of E_{04}:
2.9 eV for $x = 0.3$ and 3.6 eV for $x = 0.4$. These results contrast sharply with the much
lower optical gaps and hydrogen content of aSi$_{1-x}$C$_x$H$_y$ produced conventionally at higher
deposition power [4–7]. The SRO of these alloys is by no means experimentally settled.
Some experiments point to near chemical order [8] while others to near random [9]. The
difference in optical gaps of the two types of material may reach even 1 eV.

Since these differences occur at the same composition x, they must be due to the
differences in (i) SRO present in each type of alloy and (ii) the level of hydrogen content.

It seems therefore of value to investigate the effects of these two factors on the electronic properties of Si-rich a-SiC and in particular try to check the proposed structural model of methylated amorphous Si. For a first attempt on the properties of C rich a-SiC alloys the reader may consult [10].

A previous calculation by Martin-Moreno and Verges [11] has investigated the influence of SRO on the gap of unhydrogenated $Si_{1-x}C_x$ but quantitative contact with experiment was not possible because of the lack of an explicit account of the effects of H and also because of the chosen set of tight-binding (TB) parameters which produced an unrealistically high E_g for $Si_{0.5}C_{0.5}$ (3.4 eV). On the other hand the pioneering work of Robertson [12] (whose TB parameters we use) has revealed the general features of these alloys but his calculations were limited to the case of chemical order, although qualitative predictions on the degree of disorder were made.

Before completing this section it is worthwhile summarizing the similarities and differences of these two types of compounds i.e. those that are produced at high- and low-deposition energy. In all of these compounds the starting point (i.e. $x = 0$) is the optimized a-Si:H material with 10% of H. As the stoichiometric index x is increased the extra hydrogen is incorporated into the alloy in the form of CH_n groups [13–14]. In the case of methylated silicon one gets only CH_3 configurations with the remaining bond taken by a silicon. Hence the H content is high. In the alloys produced at higher deposition power densities the number of hydrogen NN of carbon may be smaller making room for more Si–C and C–C bonds.

2. Method

The method of Gomez-Santos and Verges [15] that we use is a direct space TB method on a Bethe lattice with a configurational averaging which includes diagonal and off-diagonal disorder (as well as valence disorder if necessary). The method is well documented by now [16, 17] so that there is no need to describe the equations for the self-energy of each type of atom. These equations depend on the conditional probability p_{AB} that an A atom has a B nearest neighbour and therefore it is very sensitive to the SRO of the system and well suited for the purposes of this calculation. We also note that in a recent application of this method to crystalline alloys it has given much better band gaps than the CPA [17].

The TB parameters are those of Robertson [12]. These parameters are—in our view— the most reliable because they not only give the correct crystalline band gaps but also the correct band-edge offsets between Si, SiC and C. However, there is a complication since Robertson has not found it possible to fit the bands of Si and SiC with a single set of Si orbital energies E_s, E_p common to both Si and SiC. This difference in E_s and E_p amounts to a Hamiltonian with parameters dependent on x and no method exists so far to account for this. The problem is not serious because the average number of C NN of Si is small (to be quantified later) since all of the extra hydrogen bonds preferentially to C. However we have taken account of this complication and have scaled, at each x, the diagonal elements of Si by the relevant probability p_{SiC} of finding a carbon NN of Si.

It is also necessary to adjust one of the Si–Si hopping matrix elements for the following reason. The TB parameters in [12] produce a band gap E_g for Si of 1.1 eV and indeed we get the same value (and the same band-edge offsets) when we do the calculation on a Bethe lattice. However a-Si:H with 10% of H has an $E_{04} = 1.0$ eV or 1.75 eV if a Tauc plot is used. To take account of that we have adjusted the $pp\sigma$ parameter so that $Si_{0.9}H_{0.1}$ has $E_g = 1.9$ eV. The adjustment is minor, 3.12 eV instead of 2.72 eV. The widening of the

band gap is produced in our calculation mainly by a recession of E_v in accordance with both theory and experiment. Note that the difference of 0.7–0.8 eV in the value of the gap is not only due to the 10% of H but also to the different definition of a gap in an amorphous and crystalline material. Very minor adjustments were also made for the C–C parameters to get an $E_g = 5.5$ eV. For ordered SiC we get $E_g = 2.65$ eV. No adjustments at all were made for the Si–C parameters.

We now come to the calculation of the conditional probabilities p_{AB} and the determination of the minimum number of SRO parameters. We designate the probabilities of the various bonds found in the alloy as follows: $P(\text{Si–Si}) = k$, $P(\text{Si–C}) = l$, $P(\text{C–C}) = q$, $P(\text{Si–H}) = n$ and $P(\text{C–H}) = m$.

By requiring that all atoms of each type saturate all the corresponding types of bonds we get the following three equations.

$$2k + l + n = 8x'c \tag{1}$$

$$2q + l + m = 8y'c \tag{2}$$

$$m + n = 2z'c \tag{3}$$

where the normalization constant $c = (4x' + 4y' + z')^{-1}$ and x', y', z' are the stoichiometric indices of Si$_{x'}$C$_{y'}$H$_{z'}$. For example equation (1) means that all Si atoms saturate all the Si–Si, Si–C and Si–H bonds.

It can be seen that we have three equations and five unknowns so that any two of the bond probabilities may be treated as independent parameters, i.e. our SRO parameters. We choose these to be q and m. The conditional probabilities p_{AB} can now be determined by an application of Bayes theorem. For example $p_{CH} = m/8yc$. In fact we set $p_{CH} = \alpha$ and use α instead of m for our second SRO parameter. Note that we have plenty of experimental information for α which is essentially determined by the hydrogen content z' since we always assume that 10% of H bonds to Si, unless otherwise stated. For methylated Si, $\alpha = 3/4$ ($x < 0.2$). For q, on the other hand, we have no direct experimental information but given x', y', z' and α, an upper bond may be calculated by requiring that all of the bond probabilities remain positive. A simple algebra gives:

$$q_{max} = 4y'c(1 - a). \tag{4}$$

Note that q_{max} depends primarily on the carbon and hydrogen content and to a lesser degree on x through c.

3. Results and discussion

Our calculated DOS of the ordered materials Si, SiC and C are shown in figure 1. The DOS of SiC has the characteristic 3-peak structure of an AB amorphous compound at approximately the correct energies. Those of Si and C on the other hand consist of an essentially two peak structure characteristic of the amorphous phase of monoatomic semiconductors and is produced by the Bethe lattice calculation because of the omission of long-range order. The band gaps are as previously stated.

Our results for the DOS of methylated Si for various compositions and degrees of chemical order are shown in figure 2. To substantiate the arguments better some partial or local density of states (LDOS) are given. To make contact with the results of Solomon
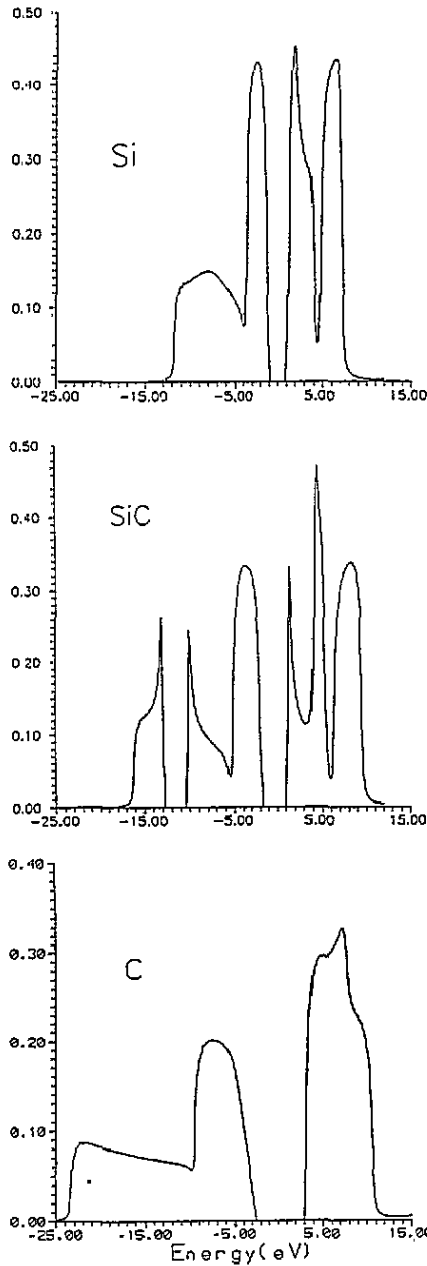
Figure 1. DOS of ordered Si, SiC and C.

and co-workers [1] we rewrite the alloy in the form $Si_{1-x}C_xH_y$. Figure 2(a) gives the DOS of $Si_{0.8}C_{0.2}H_{0.7}$ with $\alpha = 3/4$, i.e. $y = 3x + 0.1$. It can be seen that two new peaks at -19 and -11 eV have appeared which are due to the CH_3 configurations together with a just visible peak at -6 eV due to Si–H bonds. The appearance of these peaks is not new in the literature. In the calculations of Robertson two sharp peaks of equal height at these energies have appeared in the LDOS of a CH_3 cluster surrounded by stoichiometric

SiC. The interesting point is, however, the fact that the lower peak at -19 eV seems to be quenched. This was to be expected as our CH$_3$ groups are embedded in a Si-rich alloy. Pure a-Si has a zero DOS at these energies. Indeed the lowering of this peak together with the peak at -11 eV are seen in the spectra of Katayama *et al* [18]. These spectra are taken from plasma-deposited a-SiC:H samples but they can be of use as far as general features are concerned. No XPS spectra are available for methylated Si yet.

We now proceed to examine the influence of any C–C bonds. We set $x = 0.3$ and $y = 0.85 = $ the experimental value. This gives $\alpha = 0.625$ (if we still assume that only 10% of H is bonded to Si) and $q_{max} = 0.09$. We choose $q = 0.06$. These values make $p_{SiSi} > 0.8$. The DOS is shown in figure 2(b). The main change is a drastic shortening of the relative height of the peak at -11 eV. It seems that this feature is very sensitive to the presence of C–C bonds. Experimental confirmation may again be found in the spectra of Katayama *et al* [18] where this peak seems to disappear for $x > 0.25$. There, of course, the number of C–C bonds is expected to be much greater than 6%.

Next we examine the DOS of SiC alloys with a lower number of H NN of carbon. These alloys are, in general, produced at high deposition power densities and have a lower hydrogen content [7], at least for $x < 0.3$. For the moment, however, let us examine the alloy with $x = 0.3$, $y = 0.85$ 9i.e. high H content) but with $\alpha = 1.25/4$, i.e. we have moved H atoms from C–H bonds to Si–H bonds. This is shown in figure 3(a). We observe two interesting features: first the peak at -6 eV is now clearly visible because of the increased number of Si–H bonds and secondly a new peak has appeared at -14 eV. This feature is not seen as a peak in the total DOS because it merges into a plateau with the C–H peak at -19 eV but it is clearly visible as such in the LDOS of a Si atom. This feature is also seen in the spectra of Katayama *et al* as a separate peak but it was assigned to Si–CH$_3$ groups. Robertson thinks that it is due to Si–C bonds. We will see below that this correction is substantiated by our calculations. We simply note here that it has appeared when Si–C bonds have been increased. by shifting H from C to Si.

Figure 3(b) shows the DOS for lower hydrogen content with $y = 0.50$ at $x = 0.30$ and 10% of H bonded to Si. This gives $\alpha = 1.33/4$. The main difference compared to the DOS of figure 3(a) is a drastic reduction of the peak at -6 eV since we have correspondingly reduced the amount of Si–H bonds. Figure 3(c) gives the DOS for the same x, y and α but with $q = 0.09$ ($q_{max} = 0.18$) i.e. some Si–C bonds have been replaced by C–C bonds. The notable difference from figures 3(a) and 3(b) is the disappearance of states from the region near -14 eV. An examination of the LDOS of both C(s) and Si(s) states (not shown here) shows that they both contribute to this peak. Finally in all DOSs examined so far the highest peaks are either C(p) or Si(p).

We proceed to consider the variation of the band gap E_g with x for both types of alloys. This is shown in figure 4 together with the experimental values. The figure contains two sets of theoretical results: one for methylated amorphous Si and the other for the alloys produced at higher power. In each case the solid line represents alloys with no C–C bonds, the broken line with C–C bonds. We first examine the case of the high deposition power density alloys.

We have used the average of the experimentally measured hydrogen content [7, 19] while the value of α is deduced by assuming that only 10% of H bonds to Si and the rest bonds to C. For the broken line (the one with C–C bonds) we have used a value of q halfway between 0 and q_{max}. It can be seen that both curves can be consistent with the experimental data (taking into account their spread) but the broken line fits them quite well. It gives higher band gaps compared to the case of chemical order. Note that C–C bonds, which increase the gap, necessitate Si–Si bonds, which decrease the gap, and therefore the net affect cannot
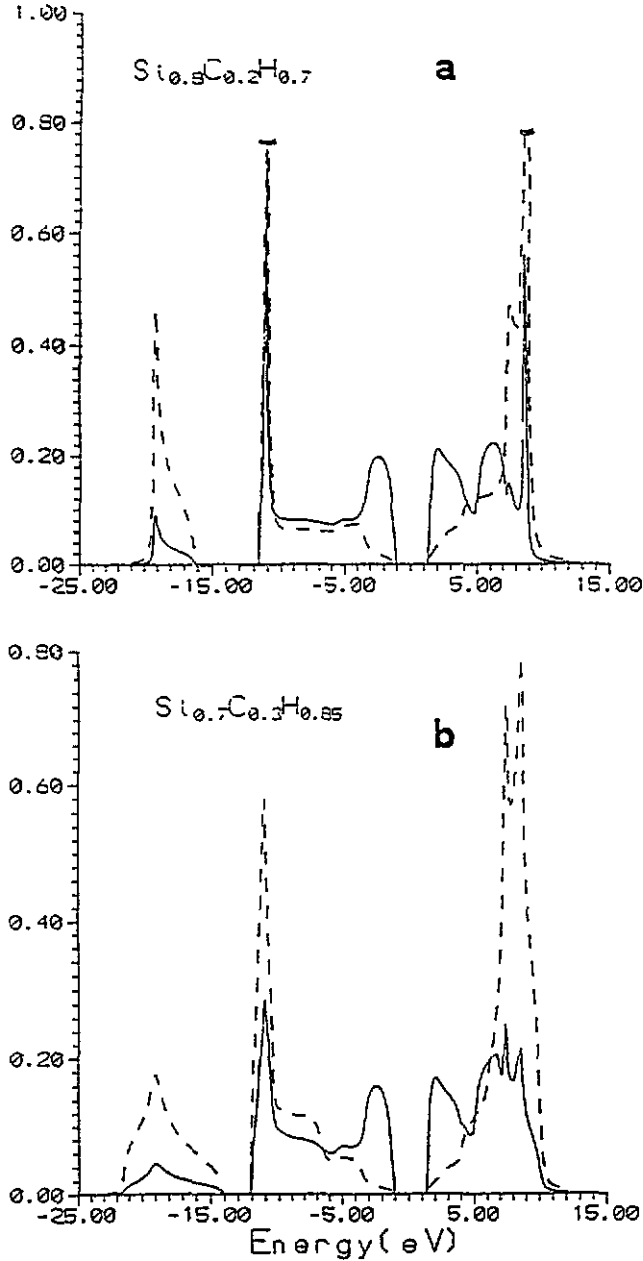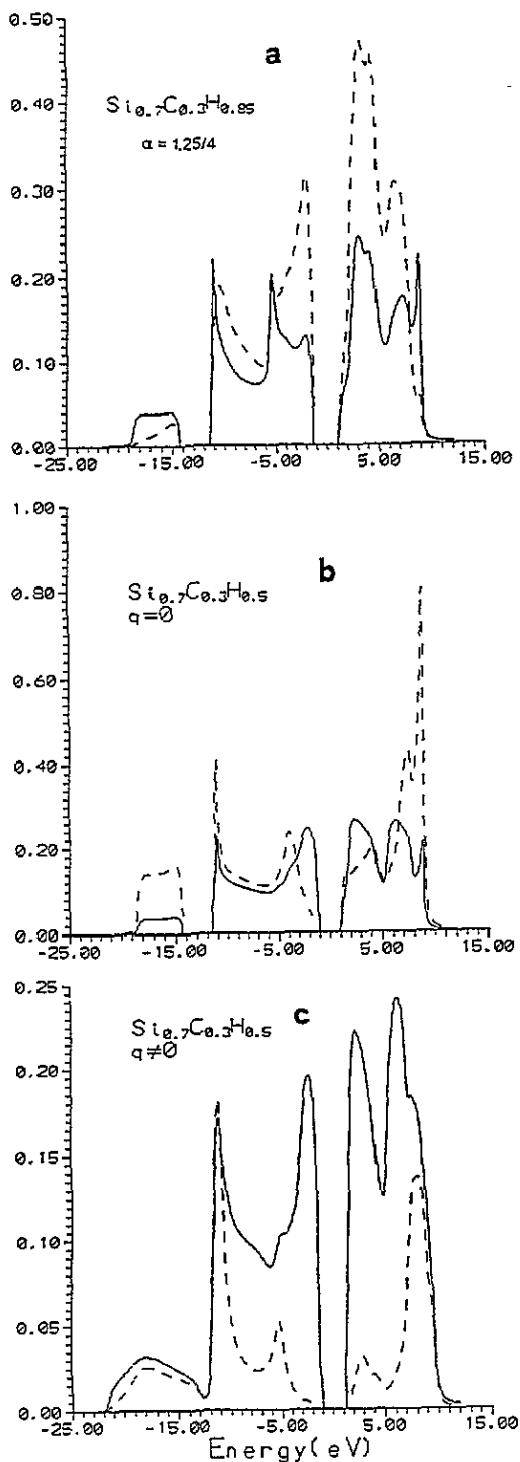
Figure 2. DOS of a $Si_{1-x}C_xH_y$ (solid line) produced at low deposition power (methylated Si) and partial DOS (broken line) of C (unweighted). (a) $x = 0.2$, $y = 0.7$, $\alpha = 3/4$, $q = 0$; (b) $x = 0.3$, $y = 0.85$, $\alpha = 2.5/4$, $q = 0.06$.

be known before the calculation is done, nor is it the same for all q and α as we will see. It must be stressed that we have made no assumption of a linearity for the variation of E_g with x. The band gap has been calculated by looking at the imaginary part of the diagonal

Figure 3. DOS of a-Si$_{1-x}$C$_x$H$_y$ produced at high deposition power (solid line) and partial DOS of either Si, C or H (broken line). (a) $x = 0.3$, $y = 0.85$, $\alpha = 1/25/4$, $q = 0$, LDOS of Si (unweighted); (b) $x = 0.3$, $y = 0.50$, $\alpha = 1.33/4$, $q = 0$, LDOS of C (unweighted); (c) $x = 0.3$, $y = 0.50$, $\alpha = 1.33/4$, $q = 0.09$, LDOS of H (unweighted).
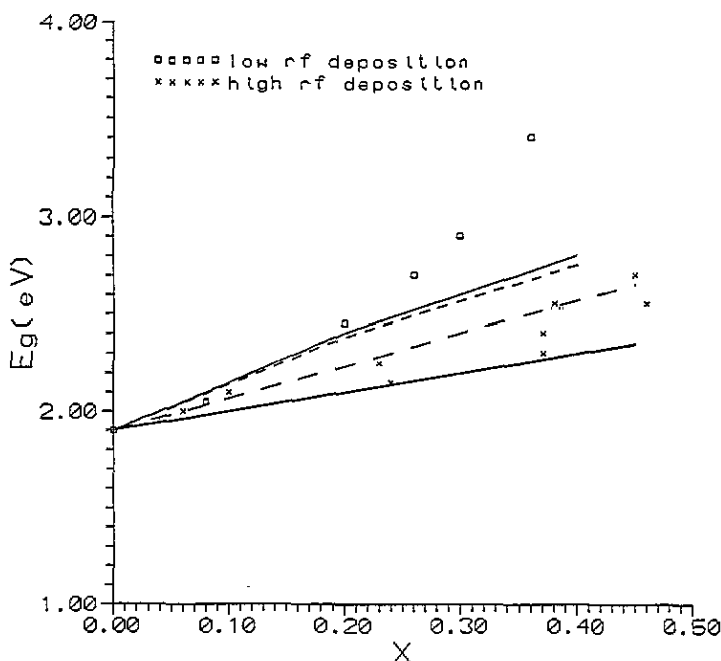
Figure 4. Variation of the band gap E_g with x: $\square$, experimental values from (1) and (3) (methylated Si); $\times$, experimental values from (4)–(7); ———: theoretical values for methylated Si with no C–C bonds; ———: theoretical values for 'high power' a-$Si_{1-x}C_xH_y$ with no C–C bonds; ----: theoretical values for methylated Si with 6% of C–C bonds; – – –: theoretical values for 'high power' a-$Si_{1-x}C_xH_y$ with 9% of C–C bonds.

Green function. We are led to tentatively suggest that a small to medium number of C–C bonds may be present depending on the preparation conditions. Our reservation is due to the fact that E_g is not very sensitive to q because of the compensation effects due to Si–Si bonds.

The remaining pair or curves gives the variation of $E_g(x)$ of methylated Si. The hydrogen content for $x < 0.3$ is that of Solomon *et al* [1]. It gives $\alpha = 3/4$ for $x < 0.20$ and $\alpha < 3/4$ for $0.2 < x < 0.3$. No data are available for $x > 0.3$. We have assumed that it saturates at $y = 0.85$ for $x > 0.3$ as it seems from the published data in the region $0.2 < x < 0.3$ [1]. The agreement of the solid line (no C–C bonds) with the measured gaps is more satisfactory for $x < 0.2$ when $\alpha = 3/4$. For $x > 0.3$ however the discrepancy is large and can not be accounted for, in our view, by any errors in the TB parameters or the method. One possibility is that it may be due to the presence of C–C bonds. The inclusion of a medium number of C–C bonds, however, gives a lower band gap and makes the disagreement worse. As a hint to this problem we have calculated the band gap of the chain structure compounds $SiCH_2$ and $SiCH_4$. The first has a gap of 3.2 eV and the second 5 eV. It may be that the low deposition power alloys with $x \approx 0.4$ possess mixed $SiCH_4$ and $SiCH_4$ chains dispersed in a Si matrix. No definite conclusions can however be drawn and no further calculations undertaken before more experimental results are available— especially the hydrogen content—in the range $0.25 \leqslant x \leqslant 0.40$. We are led to believe that the model of methylated Si is valid for $x < 0.25$ but may require modification for higher x.

4. Conclusions

We have calculated the configurationally averaged DOS of Si$_{1-x}$C$_x$H$_y$ alloys in terms of the compositional indices and SRO parameters. By examining the variation of the DOS with respect to the SRO parameters at given compositions we were able to deduce the origin of all peaks in the spectra of Katayama *et al* [18] including the peak at -14 eV which arises naturally in our calculations.

Our calculated band gaps for the alloys produced at high deposition power density are in good agreement with experiment and point tentatively to a small to medium degree of disorder. The gaps calculated for the methylated Si phase are in remarkable agreement for $x < 0.25$ when the CH$_3$ configuration is known to prevail but high discrepancies are seen near $x = 0.4$ suggesting that the methylated Si model may require modification there.

Acknowledgments

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