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# Electronic structure of hydrogenated amorphous silicon–germanium alloys studied by x-ray photoelectron spectroscopy and soft-x-ray spectroscopy

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**Abstract.** We present a study of Si 2p and Ge 3d core levels and of the valence Si 3p and conduction Si p and Ge s,d states by, respectively, x-ray-induced photoelectron spectroscopy and soft x-ray emission and absorption spectroscopy, for hydrogenated amorphous silicon–germanium  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys with  $0.16 < x < 0.60$  prepared by the glow-discharge technique. As the Ge concentration increases, the core level distributions are gradually broadened; we attribute this effect to an increase in the local disorder by alloying. The low-binding-energy edge of the valence p distribution is shifted towards  $E_F$  while the bottom of the conduction band remains at the same energy position. Thus we clearly show that the decrease in the optical gap as  $x_{\text{Ge}}$  increases is only due to a shift of the valence band edge. At the bottom of the conduction band, Si p and Ge s,d empty states are totally mixed; a spreading of the edge is observed as the Ge concentration increases. Eventually, the x-ray emission of a core excitonic state is observed as a faint structure in the Si  $K\beta$  spectra, for  $x_{\text{Ge}} = 0.45$  and 0.60.

## 1. Introduction

Hydrogenated amorphous silicon–germanium alloys ( $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ ) have given rise to much interest in recent years as possible materials for solar applications. As the Ge incorporation in the hydrogenated amorphous silicon ( $a\text{-Si:H}$ ) network is known to decrease the optical gap almost linearly, an optimized value for the gap can be obtained by the adjustment of the alloy composition. A large amount of work has been devoted to the study of the physical properties of these alloys. They have revealed that their photoelectronic properties deteriorate, compared with those of  $a\text{-Si:H}$ , as Ge is incorporated, owing to an increase of Ge-related defect states and to the development of a heterostructure in the material [1].

For samples prepared by the RF glow-discharge method in well controlled conditions [2], combined optical and photothermal deflection spectroscopy (PDS) measurements [3] have shown that the gradual decrease in the optical gap as the Ge content increases is accompanied by an increase in the inverse slope of the optical edge and by an increase in the sub-band-gap absorption which suggests the presence of a defect-related peak in the density of states (DOS) in the pseudo band gap. These results are in good agreement with recent time-of-flight (TOF) experiments [4] performed on similar alloys which evidence a widening of the conduction band (CB) tail and an increase

in the density of deeper states as the Ge concentration increases. The broadening of the CB tail seems to be related to the increase in disorder as Ge is incorporated. A study of hydrogen incorporation by thermal effusion for these a-Si<sub>1-x</sub>Ge<sub>x</sub>:H alloys [5] has shown that Ge incorporation favours the presence of weakly bonded H with respect to the tightly bonded H; the weakly bonded H is relatively unstable and associated with the porosity of the material.

We report in this paper complementary results concerning the electronic structure of the same type of a-Si<sub>1-x</sub>Ge<sub>x</sub>:H samples, obtained both by soft-x-ray emission spectroscopy (SXES) and soft-x-ray absorption spectroscopy (SXAS) and by x-ray photoelectron spectroscopy (XPS). SXES and SXAS are valuable methods for probing the local DOS of a selected symmetry; x-ray emission and absorption spectra give, respectively, the valence and the conduction states. By this method we have investigated the valence 3p states around Si atoms via the study of the Si K $\beta$  x-ray emission band (3p  $\rightarrow$  1s) in a series of a-Si<sub>1-x</sub>Ge<sub>x</sub>:H alloys for a Ge content range  $x = 0-0.60$ . As far as the conduction states are concerned, we have obtained information for the same alloys on both Si p and Ge s,d empty states from, respectively, Si K photoabsorption (1s  $\rightarrow$  np) and Ge L<sub>3</sub> photoabsorption (2p<sub>3/2</sub>  $\rightarrow$  ns,d) spectra; in that case, the spectrum from pure hydrogenated amorphous germanium a-Ge:H was also investigated. In each case, the energy scale is calibrated by reference to the Fermi level owing to the determination of the binding energy of the core level involved in the x-ray transition considered. Let us note that it is not possible to investigate with good accuracy the s valence states around Ge atoms from the Ge L emission spectrum (4s  $\rightarrow$  2p<sub>3/2</sub>) as this x-ray transition is energetically too close to the intense atomic line Ge L $\beta$ 1 (3d  $\rightarrow$  2p<sub>1/2</sub>).

The information obtained from x-ray spectra is quite complementary to that given by optical measurements which probe the band edges via band-to-band transitions.

In addition to these soft-x-ray spectroscopy (SXS) measurements, we have investigated by XPS, for the same samples, the Si 2p and Ge 3d core level distributions which can give information on the local structure and the chemical bonding in the alloys as their composition varies. Preliminary results on this work have been presented, together with optical and PDS measurements performed on the same alloys [3].

## 2. Experimental details

The a-Si<sub>1-x</sub>Ge<sub>x</sub>:H alloys were prepared by the glow-discharge technique in the ARCAM reactor under well controlled conditions [2]. The gas mixture, composed of silane (SiH<sub>4</sub>) and germane (GeH<sub>4</sub>) diluted in hydrogen, is adjusted in order to obtain various alloy compositions. A series of samples were prepared with a substrate temperature  $T_s$  of 150 °C; their Ge contents, measured by electron microprobe and by Rutherford backscattering measurements, were  $x_{Ge} = 0.16, 0.36, 0.45$  and  $0.60$ . A pure a-Ge:H sample was also prepared in similar conditions for comparison. In order to investigate the effect of substrate temperature, samples with  $x_{Ge} = 0.16$  and  $0.60$  were prepared at  $T_s = 250$  °C. The hydrogen concentration in the films deduced from electron recoil detection experiments was 15–20%.

The samples studied by XPS, SXES and SXAS were deposited simultaneously with a thickness of 1  $\mu$ m onto Mo, Al and thin Be substrates. For XPS experiments, the sampled depth is only a few tens of ångströms whereas in SXS measurements a thickness of about 0.3–1  $\mu$ m contributes to the spectrum and the data thus concern the bulk properties.

The x-ray experiments were performed in a bent-crystal vacuum spectrometer [6] equipped with gypsum or beryl crystals, giving a total instrumental broadening of, respectively, 0.25 eV and 0.30 eV in the spectral ranges of the Si K and Ge  $L_3$  spectra. We evaluate the energy uncertainty to be about 0.1–0.2 eV.

The photoelectron spectra of Si 2p and Ge 3d core levels were induced with monochromated Al  $K\alpha$  radiation for which the total instrumental broadening is about 0.5 eV. An energy uncertainty of 0.1 eV is obtained. The energy scale is calibrated by reference to the C 1s line taken at 285 eV.

### 3. Results and discussion

#### 3.1. Core levels

The Si 2p and Ge 3d core level distributions have been studied for  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys with  $x = 0.16\text{--}0.60$  and for pure  $a\text{-Si:H}$  and  $a\text{-Ge:H}$ . As the samples are not prepared *in situ*, the presence of oxygen is detected. For all the alloys the Si 2p line from  $\text{SiO}_2$  is observed at about +4 eV from that for pure Si. The Ge 3d line from  $\text{Ge}_2\text{O}_3$ , located at about +3.2 eV from the pure Ge 3d signal, is observed only for pure  $a\text{-Ge:H}$ ; in the alloys, this line is not detected, within the limit of the experimental accuracy. These results clearly show that there is a preferential oxidation of Si atoms in  $a\text{-Si-Ge:H}$  alloys. The same conclusion was recently deduced in [7] from the study of  $a\text{-Si-Ge:H}$  alloys prepared by the glow-discharge method; moreover it was concluded from the XPS profile that the oxidation does not exceed a superficial layer 5 nm thick.

Both Si 2p and Ge 3d lines remain at the same energy as  $x$  varies, within the experimental uncertainties. This result is consistent with the fact that Si and Ge atoms have approximately the same electronegativity and that, consequently, charge transfer upon alloying remains negligible. This is in agreement with previous results [8, 9] but is not consistent with the recent measurements in [7] which show a small energy shift of both Ge 3d and Si 2p towards high binding energies as  $x_{\text{Ge}}$  increases. However, the distance between the two lines remains the same and the possible effect of energy calibration cannot be totally excluded in that case.

Our measurements reveal slight broadening of the lines with increasing Ge concentration. The effect is more significant for Ge 3d than for Si 2p. Figure 1 displays the Ge 3d line for  $x = 0.16$  and 0.60; the broadening is about 6% as  $x_{\text{Ge}}$  increases from 0.16 to 0.60 and occurs on both sides of the line. Consequently it cannot be attributed totally to a possible oxidation effect which would lead to a spreading of Ge 3d at the bottom of the high-energy side of the line. We interpret this result as due to an increase in the local charge fluctuations around Ge atoms as the Ge concentration increases, which reveals an increase in the local disorder. As Ge is incorporated in the amorphous network, Si–Ge and Ge–Ge bonds are gradually formed; extended x-ray absorption fine-structure (EXAFS) measurements performed on similar alloys have shown that the lengths of Si–Ge and Ge–Ge bonds are, respectively, 2.38 Å and 2.45 Å and that they do not vary with the composition [10], which implies a progressive distortion of the amorphous network. The fact that the disorder effect is more important for Ge 3d than for Si 2p could be attributed to a less effective compensation of defects around Ge atoms than around Si atoms owing to the preferential attachment of hydrogen to Si atoms.

#### 3.2. Valence band

The Si  $K\beta$  ( $3p \rightarrow 1s$ ) emission observed from  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys with  $x$  varying from 0.16 to 0.60, and  $T_s = 150^\circ\text{C}$  are presented in figure 2, together with the K photo-

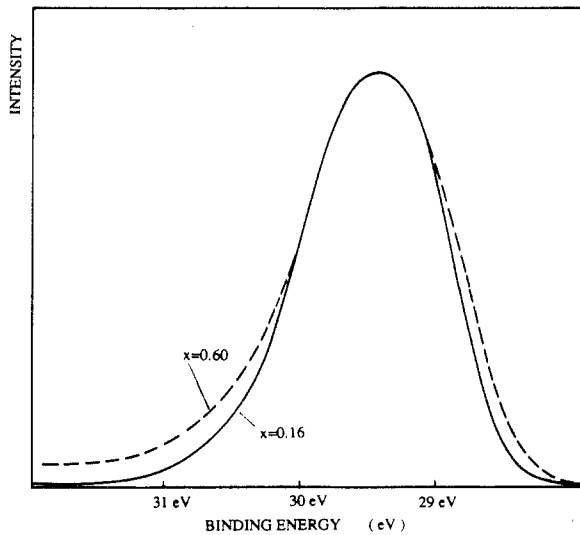


Figure 1. Ge 3d line from a-Si<sub>1-x</sub>Ge<sub>x</sub>:H alloys with  $x = 0.16$  (—) and  $0.60$  (----).

absorption spectra ( $1s \rightarrow np$ ). The amplitudes of the experimental curves are arbitrarily normalized.

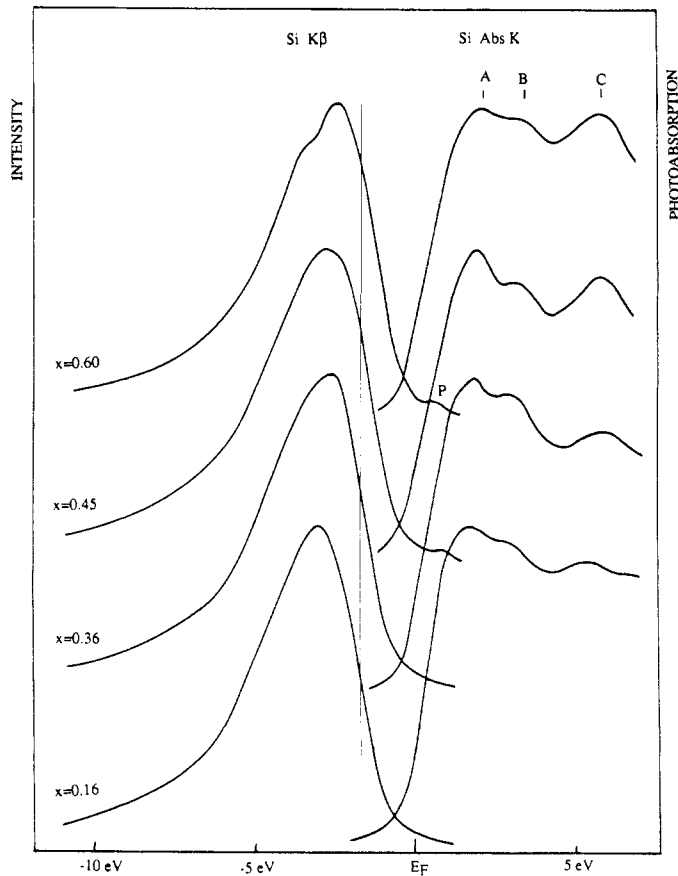
For each alloy, the emission and absorption spectra are obtained as a function of the transition energy. As they correspond to electronic transitions involving the same core level (Si 1s), the energy scale is the same for both spectra. The position of the Fermi level is set on this energy scale by means of the Si 1s binding energy value obtained as reported previously [11] from combined XPS measurements of Si  $2p_{3/2}$  binding energy and SXES measurements  $2p_{3/2} \rightarrow 1s$  ( $K\alpha$ ) transition energy. In these conditions, the spectra from the different alloys can be compared on the same energy scale with  $E_F$  as reference. This adjustment is presented in figure 2.

The Si  $K\beta$  spectra correspond in a first approximation to the convolution product of the Si p DOS of the valence band (VB) with the Lorentzian distribution of the Si 1s core level which is about 0.45 eV wide. Thus the fine structures of the DOS are smoothed out. However, as the width of the core level distribution remains small compared with the VB distribution, we consider that the Si  $K\beta$  spectrum gives a fair account of the 3p distribution around Si atoms. By comparison with the x-ray-induced photoelectron spectra of the VB corresponding to the total VB distribution, it appears that the Si  $K\beta$  spectra reflect the total p distribution of the VB band; this is the consequence of the covalent character of the bond. As  $x_{Ge}$  increases, the following results are observed.

(i) The low binding-energy edge of the emission band is gradually shifted towards  $E_F$  with almost no change in the slope of the edge. The shift, measured at half-maximum of the edge, is +0.5 eV for  $x_{Ge} = 0.6$  compared with pure a-Si.

(ii) The general shape of the distribution remains approximately the same as  $x_{Ge}$  is incorporated for  $x = 0-0.45$ . For  $x = 0.60$ , a shoulder is observed at  $E_F - 3$  eV, which is not present for the lower concentrations. Furthermore a slight broadening of the curve is noted as  $x_{Ge}$  increases.

(iii) Finally, for  $x = 0.45$  and  $0.60$ , the spectrum reveals clearly the presence of a small peak P, at the bottom of the edge, at about  $E_F + 1$  eV, i.e. in the gap region.



**Figure 2.** Si  $K\beta$  emission and Si  $K$  photoabsorption spectra for  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  with  $x = 0.16\text{--}0.60$ .

A calculation of the partial and total DOSs for  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys has been performed in a tight-binding coherent-potential approximation [12]. Good agreement has been found between experimental Si  $K\beta$  spectral distributions and theoretical curves obtained by the convolution of the partial p DOS and a broadening function including the inner Si 1s level distribution and the instrumental effect [12]. For  $x = 0.60$ , the shoulder observed in the  $K\beta$  spectrum at  $E_F - 3$  eV is well predicted by the calculation. This feature results from the fact that the shapes of the p DOS are slightly different for Si and Ge; in particular for pure Ge, the low-binding-energy peak is narrower than for pure Si and the shoulder at  $E_F - 3$  eV is better resolved. For  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys, the feature becomes more marked as  $x$  increases, so that for  $x_{\text{Ge}} = 0.60$  it becomes significant whereas for a low Ge concentration it is smoothed out by the broadening function.

The most important effect observed experimentally for the p vB distribution of  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys as the Ge concentration increases is the gradual shift of the low-binding-energy edge towards the Fermi energy. As the hydrogen concentration remains almost constant, this effect must be ascribed to Ge alloying. For the same alloys, the optical gap  $E_{04}$  (defined as the energy at which  $\alpha = 10^{-4} \text{ cm}^{-1}$ ) has been determined from accurate measurements of the optical absorption coefficient spectra  $\alpha(h\nu)$ ;  $E_{04}$

decreases linearly as  $x_{\text{Ge}}$  increases, following  $E_{04} = 1.92 - 0.67x$  [13]. As previously noticed, the distance  $\delta E_V$  measured between the VB edge and  $E_F$  in our experimental spectra decreases with increasing  $x$  at approximately the same rate as  $E_{04}$ . As almost no shift of the CB edge is detected from the photoabsorption Si K edge (see below), we conclude that the narrowing of the optical gap in these alloys is essentially due to a shift of the top of the VB towards lower binding energies.

The effect of the substrate temperature  $T_s$  has been studied for two Ge concentrations: 0.16 and 0.60. At low Ge content, the increase in  $T_s$  from 150 to 250 °C is accompanied by a slight steepening of the top of the  $K\beta$  emission spectrum and a faint decrease in intensity in the region  $E_F - 7$  eV. For  $x = 0.60$ , the steepening effect at the top of the 3p distribution is also observed as  $T_s$  increases and an attenuation of the shoulder at  $E_F - 3$  eV is noted. The steepening of the edge, leading to a shift of the maximum towards lower binding energies, reveals that more states are present at the top of the VB for  $T_s = 250$  °C than for 150 °C; these additional states can be attributed to an increase in disorder of the network at 250 °C relative to 150 °C, and especially to larger dihedral angle fluctuations [14]. The slight decrease in intensity observed, as  $T_s$  increases, at about  $-7$  eV, which corresponds to the sp states, can be interpreted by referring to previous studies of the a-Si:H VB distribution [15, 16], to a better local ordering for low- $T_s$  alloys.

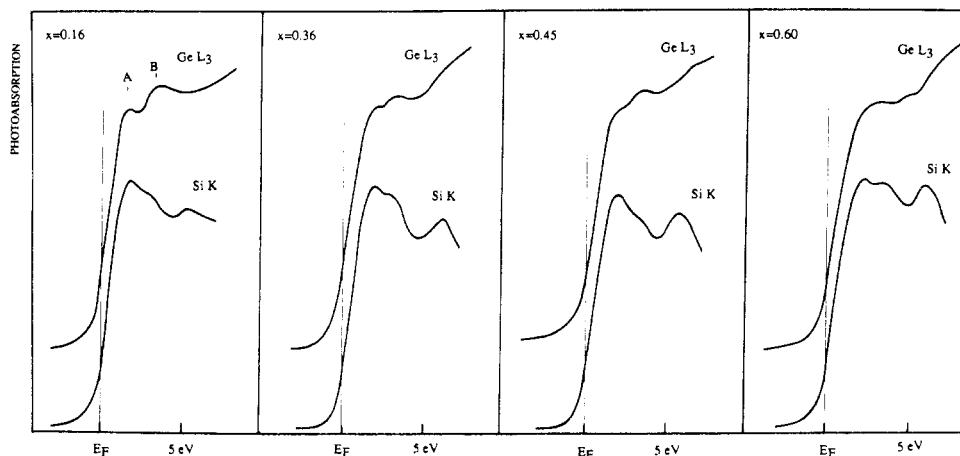
### 3.3. Conduction band

The photoabsorption spectra near the Si K edge, which are plotted in figure 2, correspond in a first approximation to the variation in the p-symmetry unoccupied DOS around Si atoms broadened by the Si 1s core level distribution. As detailed above, the spectra are given in the same energy scale as the Si  $K\beta$  emission spectra, with  $E_F$  as reference.

From these curves, we deduce that the limit of the Si p conduction states remains almost at the same distance from  $E_F$  for a-Si $_{1-x}$ Ge $_x$ :H as the Ge concentration increases. Beyond the edge, structures denoted A, B and C are observed at about 1.7 eV, 3.0 eV and 5.5 eV, respectively, from  $E_F$  for  $x = 0.16$ . As  $x_{\text{Ge}}$  increases, a spreading of the edge is observed. It involves a progressive shift of A away from  $E_F$ ; similarly B and C are shifted by about the same amount. For  $x = 0.60$ , the shift is about +0.5 eV compared with  $x = 0.16$ . Moreover the structures become more and more contrasted.

It has been experimentally possible to probe also the Ge conduction states by analysing the photoabsorption spectra at the Ge  $L_3$  edge for the same alloys. These spectra are reported in figure 3 (upper curves) for  $x_{\text{Ge}} = 0.16, 0.36, 0.45, 0.60$  and  $T_s = 150$  °C. The position of  $E_F$  on the energy scale is determined by means of the Ge  $2p_{3/2}$  binding energy value; it should be noted that this energy remains approximately constant as the alloy composition varies. These experimental curves correspond to the convolution of the s,d empty DOS around Ge atoms by the Lorentzian distribution of the Ge  $2p_{3/2}$  level which is 0.8 eV wide [17]. In figure 3, the Si K photoabsorption spectra (lower curves) are given on the same energy scale with  $E_F$  as reference. The amplitudes of the two series of curves are arbitrarily normalized on each side of the edge.

It appears from this figure that the Ge  $L_3$  edge remains almost at the same energy as  $x_{\text{Ge}}$  varies. Beyond the edge, two features are observed at about  $E_F + 1.8$  eV and  $E_F + 3.5$  eV, followed by an increase in the curve. A spreading of the edge occurs from 0.16 to 0.60. This effect remains slight for  $x \leq 0.45$  and is more marked for  $x = 0.60$ . It is accompanied by a slight shift of the first absorption maximum A away from  $E_F$ . The



**Figure 3.** Si K and Ge  $L_3$  photoabsorption spectra from  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys adjusted on the energy scale by reference to  $E_F$ .

effect is amplified for pure  $a\text{-Ge:H}$ . As mentioned above, the spreading is also observed for the Si K edge; however, the effect is less important than for the Ge  $L_3$  edge.

From the adjustment of the experimental curves presented in figure 3, the relative positions of the Si p and Ge s,d empty conduction states are directly obtained by reference to  $E_F$ . It appears that for each alloy the bottoms of the Si K and Ge  $L_3$  edges are at the same energy, which indicates that empty Si p and Ge s,d states are both present at the bottom of the CB for  $x$  varying from 0.16 to 0.60. Beyond the edge, the peaks A and B are approximately at the same energy positions for Si p and Ge s,d distributions, but their relative intensities are reversed. Thus the density of s,d states increases beyond  $E_F$  while the density of p states has a maximum at the bottom of the CB. In agreement with our results, DOS calculations mentioned above [12] predict that s and p states are present at the bottom of the CB, p states being predominant.

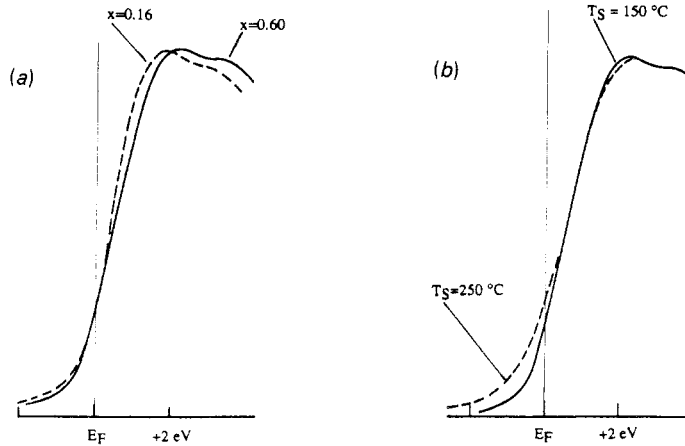
The spreading of the Si K and Ge  $L_3$  edges can result either from a broadening of the core level involved in the absorption transition or from a spreading of the CB edge. The broadening of the core level distributions Si 1s and Ge  $2p_{3/2}$  can be expected to be of the same order as that occurring for Si 2p and Ge 3d core levels; so this effect cannot explain the experimental data. As a consequence, the experimental results show that the CB edge is broadened as  $x_{\text{Ge}}$  increases. The effect is more significant for Ge s states than for Si p states. This broadening can be related to potential fluctuations due to an increase in geometrical disorder—topological and quantitative disorders—as Ge is incorporated. The increase in disorder as Ge is incorporated is also evidenced by our XPS measurements.

It should be noted that the broadening of the CB edge has also been deduced recently from TOF experiments performed on similar  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys [4].

It is noteworthy that the effect of disorder occurring as  $x_{\text{Ge}}$  increases is significant at the CB edge where both s and p empty states are present while no effect is detected at the VB edge where quasi-pure p states are found. This reveals that the sp hybridized anti-bonding states are more sensitive to disorder than pure-p bonding states.

These results are in very good agreement with recent calculations of the electronic DOS at the band edges of  $a\text{-Si}$ , made for two continuous distorted networks [18]. These calculations show that the CB edge is more sensitive to the structural disorder than is the





**Figure 4.** Si K photoabsorption edge: (a) influence of  $x_{\text{Ge}}$  ( $T_s = 150^\circ\text{C}$ ); (b) influence of  $T_s$  ( $x_{\text{Ge}} = 0.6$ ).

VB edge, because s and p states are mixed at the bottom of the VB while quasi-pure p-like states are present at the top of the VB. Let us recall that, for the valence states, the effect of structural disorder induces modifications of the electronic DOS essentially in the region corresponding to the hybridized sp states [19].

The effect of substrate temperature observed for 60% Ge alloys is presented in figure 4(b) for the Si K edge, and the effect of alloying in figure 4(a). The increase in  $T_s$  from 150 to 250 °C is accompanied by a spreading of the absorption edge, especially at the bottom of the edge; a similar effect is observed at the Ge  $L_3$  edge. It is noteworthy that the effect of an increase in  $T_s$  on the CB edge is quite different from the alloying effect resulting from the incorporation of Ge in the a-Si matrix. In the case of an increase in  $T_s$ , a spreading of the edge occurs in particular near and below  $E_F$ ; it can be correlated to an increase in the density of gap states located near the CB edge, due to an increase in disorder-induced defects. On the contrary, in the case of an increase in  $x_{\text{Ge}}$ , the spreading occurs mostly in the upper part of the edge; it corresponds to a broadening of the CB edge induced by the increase in disorder as discussed previously and to a modification of the distribution of the empty states due to the alloying effect.

### 3.4. Gap region

The structure P which is observed at the bottom of the high-energy edge of the  $K\beta$  emission spectra for  $x_{\text{Ge}} = 0.45$  and 0.60 (figure 2) is located in the energy region of the band gap, beyond  $E_F$ .

In a previous study of the x-ray spectra of a-Si<sub>1-x</sub>Ge<sub>x</sub>:H alloys, prepared in different conditions, we had noticed the presence of a shoulder located at the bottom of the high-energy edge of Si  $K\beta$ , close to the top of the VB, for high Ge concentrations [15]. Its intensity increased with increasing  $x_{\text{Ge}}$  and its energy position remained unchanged. We interpreted this structure as localized states of p symmetry in the pseudo-gap near the VB edge due to a high defect density. The existence of these states was also evidenced by a study of the optical absorption edge in the same samples [20].

In the present case, the feature P does not have the same characteristics. It is well resolved from the bottom of the Si  $K\beta$  edge and its energy position depends on the alloy composition. In both cases, it is located close to the bottom of the CB; it is possible to attribute this low-intensity peak to the radiative decay of a core excitonic state having a p character. In order to estimate the distance  $E_{\text{ex}}$  from the exciton to the CB, we locate the top of the VB by extrapolation of the linear part of the Si  $K\beta$  top edge and take into account the value of the energy gap for each alloy;  $E_{\text{ex}}$  is about 0.2 eV and 0.4 eV for  $x_{\text{Ge}} = 0.45$  and 0.60, respectively. The presence of this excitonic state is expected to contribute to the broadening of the bottom of the absorption Si K edge as observed.

The relative intensity of this excitonic peak is about 1% for  $x_{\text{Ge}} = 0.45$  and increases slightly with increasing Ge content. It is probably too low to be detected for lower Ge concentrations. Evangelisti *et al* [21] reported core excitonic effects in amorphous silicon-carbon (a-Si-C) alloys from combined Si 2p photoelectron spectra and partial-yield photoemission spectra and concluded that the core exciton binding energy increases with increasing degree of disorder, which is in agreement with our observations.

For the same alloys, PDS measurements have revealed the presence in the pseudo-gap of additional states near the VB edge as  $x_{\text{Ge}}$  increases [3]. These states are attributed to Ge-related defect states, in correlation with the increase in spin density as the Ge concentration increases [13]; they are not detected clearly in the Si  $K\beta$  emission spectra, which confirms that they are associated with Ge states.

It should be noted that x-ray emission from core excitons in semiconductors has recently been reported in the Al  $K\beta$  spectrum of AlAs [22]. It has also been evidenced in the Si L spectra of crystalline silicon (c-Si), amorphous silicon (a-Si) and a-Si:H [23]. In the latter case the exciton intensity is found to vary approximately as  $E_{\text{ex}}^2$ .

#### 4. Conclusion

The electronic structure of  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys prepared by the glow-discharge method has been studied experimentally by SXES, SXAS and XPS. As Ge is incorporated in the a-Si network, our results show that the top of the VB which consists of bonding p states is progressively shifted towards the Fermi level, whereas the bottom of the CB remains at the same energy. As a consequence, we conclude that the decrease in the optical gap  $E_G$  occurring as  $x_{\text{Ge}}$  increases is essentially due to a shift of the VB. Good agreement is found between the energy shift of the VB and  $\delta E_{04}$ -value for  $x_{\text{Ge}}$  varying from 0 to 0.6.

Unoccupied states around Si and Ge sites have been investigated from the analysis of the photoabsorption spectra near the Si K and the Ge  $L_3$  edges, respectively. Our results reveal that empty Si p and Ge s,d states are both present at the bottom of the CB of the alloys. A broadening of the CB edge is clearly observed as  $x_{\text{Ge}}$  increases, for both Si p and Ge s,d distributions. We interpret this spreading as an increase in disorder in the alloy network as Ge is incorporated. On the contrary, the slope of the VB edge is unaffected by alloying. These results clearly indicate that mixed sp anti-bonding states located at the bottom of the CB are more sensitive to disorder than are pure-p bonding states which are present at the top of the VB.

It should be noted that the increase in disorder as Ge is incorporated is also evidenced from the gradual broadening of the core level distributions Si 2p and Ge 3d. The fact that the broadening is more marked around Ge atoms than around Si atoms is attributed to a less effective compensation of defects around Ge atoms due to the preferential attachment of hydrogen to Si atoms. The increase in disorder as Ge is alloyed to Si, also

revealed by the study of the band edges by PDS [3] and TOF [4] experiments performed on a-Si-Ge:H samples prepared in the same conditions, probably contributes to the deterioration of the photoelectronic properties of the alloys as Ge is incorporated.

Finally, we observe for  $x_{\text{Ge}} = 0.45$  and  $0.60$  a faint structure on the Si  $K\beta$  emission which we attribute to the presence of an excitonic state.

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