Auger electron (AES), electron energy loss (EELS) and X-ray photoelectron spectroscopy (XPS) were used to identify the reaction products at the fibre-matrix interface in SiC nicalon fibre-LAS (Li$_2$O, Al$_2$O$_3$, SiO$_2$) or LAS+Nb$_2$O$_5$ glass matrix composites. Chemical bonding of the different elements was investigated by AES using sputter-depth profiling on fibres extracted from two matrices by etching in hydrofluoric acid. The chemistry of the silicium was studied by EELS in nicalon-LAS+Nb$_2$O$_5$ composite cross-sections. XPS was performed on fibres extracted from the nicalon-LAS+Nb$_2$O$_5$ composite to confirm EELS and AES results. These investigations show that in both composites the reaction scale at the fibre-matrix interface consists of a carbon layer next to the matrix and of a silicate phase rich in oxygen which contains carbon, probably in the form of a silicon oxycarbide, and which is located between the carbon layer and the fibre core.

1. Introduction
The compositional characteristics of two interphases previously identified by high resolution transmission electron microscopy (HRTEM) [1] in SiC nicalon fibre Li$_2$O, Al$_2$O$_3$, SiO$_2$-LAS glass matrix composites were described in Part I of this article. The phase composition of the layer next to the matrix, the carbon layer (CL), is well established and confirms previous results [2-5]. The analyses suggest that the transition region (TR), which lies between the carbon layer and the fibre core, contains a silicate phase rich in oxygen, and the amount of this phase is highest next to the CL.

The aim of this paper is to identify this oxygen-rich phase formed by fibre-matrix reaction. The interphases were thus analysed using techniques which could reveal the chemical bonding of the elements detected in the TR. The chemistry of the interfacial layer was investigated by Auger electron spectroscopy (AES). AES has rather good lateral resolution ($L < 50$ nm) and good sensitivity to the chemical states of the silicon, carbon and oxygen which are found in the interphases. The AES analyses were complemented by a study of Si bonding at the CL-TR interface by electron energy loss spectroscopy (EELS) and by X-rays photoelectron spectroscopy (XPS). EELS analysis has excellent spatial resolution ($\approx 6$ nm), but may be influenced by the oxidation of thin foils. XPS has poorer spatial resolution than AES or EELS, but results in more accurate chemical information than AES and, in the case of the TR, than EELS.

2. Samples
EELS analyses were performed on cross-sections of nicalon-LAS+Nb$_2$O$_5$ composite, and the AES and XPS analyses on fibres extracted from nicalon-LAS and/or LAS+Nb$_2$O$_5$ as described in Part I. Pure $\alpha$-SiC, pure SiO$_2$ and the core of a nicalon fibre were also characterized by AES and EELS to calibrate the data.

3. AES analysis of the near surface of extracted fibres
The purpose of the Auger analysis is to characterize the chemical states of the silicon, carbon and oxygen in the interfacial region as a function of depth.
3.1. Experimental parameters

Auger electron spectroscopy was carried out on a Perkin Elmer 660 instrument. A 3 keV primary electron beam current of 30 ± 5 nA was used for Auger electron excitation. The relative energy resolution of the spectrometer was 0.6%. As for the secondary ion mass spectroscopy (SIMS) analysis, the interfacial region was characterized by sputter profiling the surface of extracted fibres. The sputtering was done with an Ar + ion beam whose energy was 3 keV and whose current density was 45 mA cm⁻². An AES analysis was performed at sputtering intervals of 1 min. The diameter of the analysed region was about 100 nm.

3.2. Choice of Auger transitions

To characterize the silicon, the LMM Auger transition was selected. Several reasons justify this choice. Firstly, the LMM transition signal of Si bonded in SiO₂ is located at about 76 eV, while the LMM transition signal of Si in pure Si is found at about 92 eV. This means that SiO₂ can be easily distinguished from unoxidized Si. Secondly, the resolution of the spectrometer, proportional to the energy, is better at lower energies (0.6 eV at 92 eV). Finally, the relative sensitivity factor for Si is much larger for the LMM transition (0.35) than for the KLL transition (0.025). For carbon and oxygen, the only available transition is the KLL. The KLL transition for carbon and oxygen is located at about 272 and 510 eV, respectively. The energy resolution of the spectrometer for each transition is given in Table I.

3.3. Calibration references

The silicon and carbon transitions were characterized in an α-SiC standard, used as a reference in the SIMS analysis. The Si–LMM and the C–KLL Auger transitions were measured after 1, 2, 3, 4 and 5 min sputtering. The transitions do not change during sputtering (Fig. 1). Therefore, it can be assumed that Ar⁺ sputtering does not induce any chemical modification in the SiC phase. The characteristics of the Si and C transitions are given in Table I. Note that the Si–LMM transition is observed at 93.1 eV in SiC.

The Si, C and O transitions were characterized in the core of a nicalon fibre (Fig. 2). The main characteristics of these transitions are shown in Table I. As in SiC, no changes in the transitions were observed during sputtering. Sputtering does not induce detectable chemical modifications of the nicalon fibre. It is important to note that a Si–LMM transition is observed at 92.7 eV, but that no signal is detected at 76 eV. The contribution of a few per cent SiO₂ present in the nicalon fibre is not detected in the Si line, thereby showing that there is a threshold to AES sensitivity in the presence of SiO₂.

The superposition of Si transitions obtained in α-SiC and in the nicalon fibre (Fig. 2a) shows that the left part of the Si transition is less abrupt in the nicalon fibre than in pure SiC and that its energy position is slightly lower, 92.7 eV instead of 93.1 eV. The nicalon fibre not only contains SiC (≈ 45 mol % [6]), but also a significant amount of SiO₂Cₓ (≈ 20 mol % [6]). Therefore, it can be assumed that these changes in the Si–LMM Auger transition line shape and energy position are due to SiO₂Cₓ, which is contained in the nicalon fibre.

Unlike the Si transition, the shape and energy position of the C–KLL transition of pure α-SiC and of the Nicalon fibre are within the resolution of the spectrometer (Table I).

3.4. Auger characterization of the transition region

3.4.1. Chemical state of the silicon

The silicon transition line shape and energy position were studied as a function of depth in fibres extracted from the nicalon–LAS and the nicalon–LAS + Nb₂O₅ composites. As an illustration, Fig. 3 shows the Si–LMM transition after increasing sputtering times for a fibre extracted from the nicalon–LAS. The Si–LMM transition is always observed at about 92 eV. In both composites, a signal located at 76 eV is observed. This is the expected energy position for SiO₂ which was never observed in the TR. Thus, as in the fibre core, the SiO₂ content in the TR does not exceed a few per cent.

In all samples, the shape and energy position of the Si–LMM transition change significantly throughout the TR before becoming stable in the fibre core. The left side of the transition becomes more abrupt and the energy position of the transition increases. In order to quantify this evolution, a reference transition, Pref, was chosen in the fibre core. As shown in Fig. 4a, the shift (S) in the energy width of the LMM transition at the half-maximum, between the left side of Pref and the left side of each Si–LMM transition was measured. S and the absolute energy position (E) versus the sputter time (t) (Figs 4b, c and 5) were then correlated. The change of S and E are both significant with respect to sensitivity of the measurement. For the fibres extracted from LAS and from LAS + Nb₂O₅, the maximum value of S is 1.5 and 1.4 eV, and the change in the energy position is about 1 and 1.1 eV, respectively; while the resolution of the spectrometer at 92 eV is 0.5 eV.

Auger analysis reveals significant evolution of the Si transition line shape and energy position throughout the TR. The reference studies performed on pure α-SiC and on the nicalon fibre suggest that this evolution is due to an increase in the SiO₂Cₓ content and a decrease in the SiC content in the TR from the fibre.

---

**Table 1** Characteristics of the AES peaks in α-SiC and in the 202 nicalon fibre. The resolution of the spectrometer for the energies characteristic of the different transitions are indicated in the table.

<table>
<thead>
<tr>
<th></th>
<th>α-SiC</th>
<th>Nicalon fibre core</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si–LMM transition</td>
<td>C–KLL transition</td>
</tr>
<tr>
<td></td>
<td>Eₘ = 93.1 ± 0.5 eV</td>
<td>Eₘ = 92.3 ± 0.5 eV</td>
</tr>
<tr>
<td></td>
<td>Wₘ = 55.3 ± 0.5 eV</td>
<td>Wₘ = 55.3 ± 0.5 eV</td>
</tr>
<tr>
<td></td>
<td>Eₘ = 93.1 ± 0.5 eV</td>
<td>Eₘ = 93.1 ± 0.5 eV</td>
</tr>
<tr>
<td></td>
<td>Wₘ = 55.3 ± 0.5 eV</td>
<td>Wₘ = 55.3 ± 0.5 eV</td>
</tr>
<tr>
<td></td>
<td>Eₘ = 93.1 ± 0.5 eV</td>
<td>Eₘ = 93.1 ± 0.5 eV</td>
</tr>
<tr>
<td></td>
<td>Wₘ = 55.3 ± 0.5 eV</td>
<td>Wₘ = 55.3 ± 0.5 eV</td>
</tr>
</tbody>
</table>

4536