Auger electron spectroscopy of compounds in the Si-Ti-C system: characterization of Si-Ti-C multiphased materials obtained by CVD

Citation for published version (APA):

DOI:
10.1016/0039-6028(93)90558-2

Document status and date:
Published: 01/01/1993

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 13. Apr. 2019
Auger electron spectroscopy of compounds in the Si–Ti–C system
Characterization of Si–Ti–C multiphased materials obtained by CVD

M. Maline a, M. Ducarroir a, F. Teyssandier a, R. Hillel a, R. Berjoan b, F.J.J. Van Loo a and W. Wakelkamp c

a IMP-CNRS, University of Perpignan, 52, Avenue de Villeneuve, F-66860 Perpignan, France
b IMP-CNRS, BP 5 Odeillo, F-66120 Font-Romeu, France
c Laboratory of Solid State Chemistry and Materials Science, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, Netherlands

Received 30 June 1992; accepted for publication 6 January 1993

Auger peak positions and line shapes analyses of the Si LVV, Si KLL, C KVV and Ti LMM transitions for reference compounds: Ti, Si, SiC, TiC, TiC_{0.32}, TiSiC_{2}, Ti_{1-2}Si_{2-4} and Ti_{1-2}Si_{2-4}C_{0.3}, belonging to the ternary Si–Ti–C system have been performed. The results show that there are sufficient differences in Auger peak positions and line shapes to allow compounds identifications. The Auger line shapes of the CKVV transitions for Ti_{1-2}Si_{2-4} and Ti_{1-2}Si_{2-4}C_{0.3} (carbon solid solution in Ti_{1-2}Si_{2-4}) were found to be characteristic of carbon bonded to titanium. The Ti L_M2,M3 transition was found to be very sensitive to changes in the nature of the compounds. The spectra recorded for the reference compounds were used to characterize Si–Ti–C multiphased materials obtained by CVD. SiC–X (X = TiSiC_{2}, Ti_{1-2}Si_{2-4}, TiC + C) mixtures were identified.

1. Introduction

Recently, increasing interest has focused on nanocomposite ceramics. As a matter of fact, due to their nanoscale structure (1–50 nm), they are expected to provide enhanced properties, specially mechanical properties, compared with composites presenting coarser structures [1–3].

Among the various techniques allowing us to prepare nanocomposite materials: sintering, hot-pressing, sputtering, sol-gel process and chemical vapor deposition (CVD), increasing interest is devoted to the last one and several examples are already found in the literature [3–5]. The high uniformity of the crystallite dispersion in the matrix and the phases obtained under near equilibrium conditions are two very attractive features encountered in CVD composite materials.

However, microchemical and microstructural investigations of this kind of materials have become more and more difficult because of the drastic reduction of the grain size, the increasing complexity of the chemical bonding system (mixture of metallic and ionic-covalent ceramics, combination of light atoms and transition elements) and also the strong imbrication of the matrix and the dispersoid structures.

Thus, characterization of nanocomposite ceramics requires cross-checking of different data obtained from complementary micro-analytical techniques.

In order to achieve the micro-chemical characterization of the Ti–Si–C codeposits prepared by CVD, electron probe microanalysis-wavelength dispersive spectroscopy (EPMA-WDS), X-ray diffraction (XRD), micro-Raman spectroscopy and Auger electron spectroscopy (AES) were undertaken [6].

Owing to the key role of the latter method, this paper is devoted to the Auger electron spectroscopy investigations.

Section 3.1 deals with Auger electron transitions corresponding to eight reference compounds in the ternary system Ti–Si–C. Their Auger spectra are reported and related to the variation of the bonding states of the elements in the ternary system.
the solid. In section 3.2, these data are compared with those obtained from the Auger spectra of CVD Ti–Si–C codeposits and phase identifications are successfully done.

2. Experimental procedure

2.1. Material preparations

Most of the materials considered in this study were prepared by CVD: SiC, TiC, TiC\textsubscript{0.72} and Ti–Si–C codeposits. Two of them: Ti\textsubscript{x}Si\textsubscript{1–x} (C) and Ti\textsubscript{3}Si\textsubscript{2} were obtained from a diffusion couple procedure. Commercial titanium foil (99.9 wt% pure), silicon ("electronic" purity) and TiSi\textsubscript{2} monocrystals were also taken into account.

Cubic SiC and Ti–Si–C codeposits were made by conventional thermal CVD, under atmospheric pressure in a classical cold wall reactor on a graphite substrate heated by joule effect in the range 1100–850°C. Gaseous C\textsubscript{4}H\textsubscript{10} and SiH\textsubscript{2}Cl\textsubscript{2} diluted in H\textsubscript{2} carrier gas were used as reactants to prepare SiC. TiCl\textsubscript{4} was added to obtain Ti–Si–C materials. Further experimental details are presented in ref. [6].

TiC and non-stoichiometric titanium carbide were also prepared by CVD under atmospheric pressure. The deposition took place at a higher temperature (1600°C) on a molybdenum substrate from an initial gas mixture composed of TiCl\textsubscript{4}, CH\textsubscript{4}, H\textsubscript{2} [7,8]. The use of a low initial molar fractions of TiCl\textsubscript{4} (X\textsubscript{TiCl\textsubscript{4}} = 4 \times 10^{-3}) was required to reach large departure from stoichiometry. The C/Ti ratio was then controlled by the molar fraction of methane.

Some materials were obtained using a diffusion couple procedure [9]. Both Ti–SiC and SiC–Ti\textsubscript{5}Si\textsubscript{3} diffusion couples were prepared by hot-pressing polished slices in a vacuum furnace (1 MPa, 10\textsuperscript{-9} bar). Ti\textsubscript{5}Si\textsubscript{3} (C) which is a solid solution of carbon in Ti\textsubscript{5}Si\textsubscript{3} was obtained from the latter couple annealed for 150 h at 1250°C. The atomic composition given by EPMA-WDS was: Ti\textsubscript{0.57}Si\textsubscript{0.33}C\textsubscript{0.1}. The so-called Nowotny phase Ti\textsubscript{5}Si\textsubscript{3} (C) [10] exhibits a hexagonal structure characterized by parallel chains of [Ti\textsubscript{6}C] octahedra, each octahedron sharing two faces with adjacent octahedra. This structure belongs to the D\textsubscript{6h} \textsuperscript{3} space group.

Ti\textsubscript{3}SiC\textsubscript{2} obtained from the same procedure by annealing a Ti\textsubscript{3}Si\textsubscript{3}–SiC couple for 100 h at 1250°C, is a hexagonal ternary compound [11] still having octahedral groups [Ti\textsubscript{6}C]. The composition of this reference compound was Ti\textsubscript{0.48} Si\textsubscript{0.16}C\textsubscript{0.36} as determined from EPMA-WDS.

2.2. Auger spectroscopy conditions

The Auger electron measurements were achieved in a Riber-Cameca surface analysis system including an electron analyser MAC-2 with a 15 keV Mikrofocus HEK-15-M electron gun, and a Riber Cameca CI-50 ion gun. The following operating conditions were used: for spectra acquired in the 50–540 eV range, 3 keV primary electrons were used and the analyser resolution was fixed at 1 eV. Spectra calibrations were based upon the Ar LVV Auger peak at 211 eV without any charging effect, so that energy deviations of 1 eV or more can be attributed to a chemical shift. All the samples were submitted to the same procedure using identical parameters.

3. Results and discussion

3.1. Reference compounds

3.1.1. Auger spectra recorded in the kinetic energy range: 20–540 eV

Auger spectra, in the EN(E) mode, recorded for reference compounds are shown in fig. 1. One can observe the following Auger features:

- Si LVV (valence–valence transition) around 90 eV,
- Ar KLL around 210 eV,
- C KVV (valence–valence transition) around 270 eV,
- the TiLMM series in the range 350–450 eV, which is composed by three main transitions:
Fig. 1. Auger spectra observed for some reference compounds in the range 50–540 eV.

(1) TiL_{23} M_{45} M_{45} (valence–valence transitions) around 450 eV always of very low intensity related to the presence of few 3d electrons in titanium [12]. (2) TiL_{23} M_{23} M_{45} (core–valence transitions) around 420 eV. (3) TiL_{23} M_{23} M_{23} (core–core transitions) around 385 eV.

For these titanium series, it is well-known that rapid Coster–Kronig transitions induce the predominance of L_{3}MM Auger transitions [13,14].

The TiM_{23} M_{45} M_{45} Auger transition was not studied in the energy range 20–50 eV because its lineshape may be influenced by SiLVV emission located in the low energy side. Moreover, the TiM_{23} M_{45} M_{45} transition is a self-convolution of the titanium valence band. Therefore, the variations in the titanium valence band density of states are better resolved in the TiL_{23} M_{23} M_{45} Auger peaks.

Significant shifts of the peak positions and modification of the line shapes allow chemical state identifications.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiLVV peak position</th>
<th>Si bonding state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>88</td>
<td>Si–Si</td>
</tr>
<tr>
<td>SiC</td>
<td>87</td>
<td>Si–C</td>
</tr>
<tr>
<td>TiSi₂</td>
<td>89.5</td>
<td>Si–Ti</td>
</tr>
<tr>
<td>Ti₀.₈Si₀.₃C₀.₁</td>
<td>89</td>
<td>Si–Ti</td>
</tr>
<tr>
<td>Ti₃SiC₂</td>
<td>89</td>
<td>Si–Ti and Si–C</td>
</tr>
</tbody>
</table>

3.1.1.1. **SiLVV Auger transitions.** The SiLVV peak positions for several silicon based compounds in regards to silicon bonding states are reported in table 1. Peak positions appear to be characteristic of each bonding state of Si. Furthermore, fig. 1 reveals that the SiLVV peak recorded for SiC is broadened as compared with the corresponding peak for Si and TiSi₂.

3.1.1.2. **TiLMM Auger transitions.** For titanium based compounds, many variations in peak positions and line shapes of titanium LMM series are observed as shown in fig. 2 and table 2. The L₁M₂₃M₄₅ transitions involving valence electrons

Fig. 2. Auger TiL₁M₂₃M₂₃ and L₁M₂₃M₄₅ line shapes for some reference compounds.
of the 3d transition elements present a valence band structure for all the 3d elements, except Cu and Zn, whose LMV transitions exhibit an atomic-like shape. These changes have been related by Sawatzky [15] to the simultaneous increase of the effective interaction between the two-hole final state of the transition ($U_{\text{eff}}$), and the decrease of the valence band width ($\Gamma_v$) which arises with increasing the number of 3d electrons.

For titanium, the $L_3M_{23}M_{45}$ Auger line shape, which has a valence band structure, is expected to reflect the valence band density of states of the ionized sample.

Fig. 2 and table 2 show that the $L_3M_{23}M_{45}$ main peak for stoichiometric and non-stoichiometric TiC phases is shifted towards lower energies (415 eV) compared with pure Ti (416 eV). This shift of about 1 eV agrees with the previously reported positions of the $L_3M_{23}M_{45}$ [16, 17].

The same peak is shifted at higher energies for TiSi$_2$ (416.5 eV). The position observed for Ti$_{0.57}$Si$_{0.33}$C$_{0.1}$ and Ti$_3$SiC$_2$ is 415.5 eV. The Ti $L_3M_{23}M_{45}$ transitions are also broadened for the binary Ti, C phases and ternary Ti, Si, C phases. So it may be concluded that the width of the titanium valence band of these phases is increased as compared with pure titanium. Concerning the stoichiometric TiC, its Ti$L_3M_{23}M_{45}$ transition exhibits a line shape (fig. 3) which reflects closely the previously reported electronic structure of the stoichiometric TiC phase determined from electron spectroscopy and X-ray emission and absorption data [18]. This line shape agrees also with the valence-band spectra induced by synchrotron radiation [19].

The low intensity peak located at 406 eV can be related to the C 2s states in the valence band of TiC. The main peak, located at 414.5 eV corresponds to the structure arising from the hybridized C 2p and Ti 3d bands. For TiSi$_2$, the Ti$L_3M_{23}M_{45}$ peak is less broadened than the corresponding peak in TiC.

For Ti$_{0.57}$Si$_{0.33}$C$_{0.1}$, a strong broadening effect which is consistent with the expected presence of various bonding states of titanium is detected. Shifts are also observed for the Ti$L_3M_{23}M_{23}$ peaks located around 380 eV. This latter transition presents a two peaks structure. Jardin [20] explained it by a multiplet splitting effect due to spin interaction between the two holes in the p level at the final state and the unpaired 3d electrons. The narrower peak located at higher energy (around 385 eV) reflects this spin interaction. It is well-known that this peak is very sensitive to titanium oxidation. Its relative intensity is lowered for TiC, Ti$_{0.57}$Si$_{0.33}$C$_{0.1}$ and Ti$_3$SiC$_2$ (fig. 2). This decrease can be attributed to the decrease of the number of unpaired 3d electrons due to Ti bonding with carbon [20]. A similar behavior of the narrower peak intensity has been observed by increasing the oxidation state of Ti in the Ti-O chemical system [20, 21].

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>$L_3M_{23}M_{45}$ peak position $E_N(E)$ (eV)</th>
<th>$L_3M_{23}M_{23}$ peak position $E_N(E)$ (eV)</th>
<th>Ti bonding state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>416</td>
<td>380.5</td>
<td>Ti-Ti</td>
</tr>
<tr>
<td>TiC</td>
<td>415</td>
<td>380</td>
<td>Ti-C</td>
</tr>
<tr>
<td>Ti$_{0.72}$</td>
<td>415</td>
<td>380</td>
<td>Ti-C</td>
</tr>
<tr>
<td>TiSi$_2$</td>
<td>416.5</td>
<td>381</td>
<td>Ti-Si</td>
</tr>
<tr>
<td>Ti$<em>{0.57}$Si$</em>{0.33}$C$_{0.1}$</td>
<td>415.5</td>
<td>380</td>
<td>Ti-C and Ti-Si</td>
</tr>
<tr>
<td>Ti$_3$SiC$_2$</td>
<td>415.5</td>
<td>380</td>
<td>Ti-C and Ti-Si</td>
</tr>
</tbody>
</table>

### 3.1.1.3. CKVV Auger transitions.

As it can be seen in fig. 1, the CKVV Auger transition allows
a good discrimination between Ti-C and Si-C bonds. Indeed, the main peak positions (table 3) are very different, located at 267 eV for SiC and 269.5 eV for TiC. Moreover, in agreement with previous published spectra [22,23], the line-shapes are salient features of each compound.

In cases of Ti_{0.57}Si_{0.33}C_{0.1} and Ti_{3}SiC_{2}, positions and line-shapes of the CKVV transition furthermore reveal that the carbon is mainly bonded to titanium. For Ti_{3}SiC_{2}, this result agrees with the fact that the carbon atoms are entirely surrounded by titanium atoms into the hexagonal cell [11].

3.1.2. Auger spectra recorded in the kinetic energy range: 1606–1625 eV

SiKL_{23}L_{23} Auger transitions. The SiKL_{23}L_{23} peaks recorded for Si, SiC, TiSi_{2}, Ti_{0.57}Si_{0.33}C_{0.1} are shown in fig. 4. This transition (table 4) is shifted towards lower energies for SiC as compared with the position in pure Si (1617.5 eV) and towards higher energies for TiSi_{2} and Ti_{0.57}Si_{0.33}C_{0.1} (1618.5 and 1618 eV, respectively). For Ti_{3}SiC_{2}, the SiKL_{23}L_{23} transition presents a very low intensity. Therefore, its position was submitted to a large uncertainty. The chemical shift observed for SiC is in good agreement with that previously reported [24].

The SiKL_{23}L_{23} peaks of SiC, TiSi_{2} and Ti_{0.57}Si_{0.33}C_{0.1} are also broadened. The peak concerning the last compound is asymmetric, suggesting the presence of various Si bonds in that phase. However, it seems that Si-Ti bonds prevail (position at 1618 eV).

From the classical kinetic energy of the electrons emitted after a KL_{23}L_{23} core levels transition:

\[ E_{KL_{23}L_{23}} = E_{K} - E_{L_{23}} - E_{L_{23}} - U_{\text{eff}}, \]

the kinetic energy changes, due to the modifications of the Si environment, can be expressed as:

\[ \Delta E_{KL_{23}L_{23}} = - \Delta E_{L_{23}} - \Delta U_{\text{eff}} \]

assuming that \( \Delta E_{K} \approx \Delta E_{L_{23}} \). \( \Delta U_{\text{eff}} \) is the variation in the effective Coulomb interaction of the two holes on the Si_{L_{23}} levels [25]. From the simple charge potential model [26], \( E_{L_{23}} \) increases while the valence electron density on silicon decreases, that is the electronegativity of the element bonded to Si. Therefore, neglecting the

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiKL_{23}L_{23} peak position EN(E)</th>
<th>Si bonding state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1617.5</td>
<td>Si–Si</td>
</tr>
<tr>
<td>SiC</td>
<td>1615.5</td>
<td>Si–C</td>
</tr>
<tr>
<td>TiSi_{2}</td>
<td>1618.5</td>
<td>Si–Ti</td>
</tr>
<tr>
<td>Ti_{0.57}Si_{0.33}C_{0.1}</td>
<td>1618</td>
<td>Si–Ti</td>
</tr>
</tbody>
</table>
variations of $U_{\text{eff}}$, it can be expected that $E_{\text{KL}23-L_{23}}$ will be shifted towards lower energy for SiC and higher energy for TiSi₂ compared to pure Si, because of the decreasing electronegativity from C to Si and from Si to Ti.

Furthermore, for a given element, the $U_{\text{eff}}$ values are dependent on the extra-atomic relaxation energies at the final state. From SiC to Si, considering the same covalent nature of the bond, small variation in $U_{\text{eff}}$ is expected. Whereas, for TiSi₂, because of the Ti3d delocalized electrons, the $U_{\text{eff}}$ value could decrease compared to Si, giving rise to a complementary contribution in the increase of $E_{\text{KL}23-L_{23}}$.

### 3.2. CVD coatings

Many multiphased materials of controlled composition were prepared in the Ti–Si–C ternary system by selecting both the initial gas mixture composition ($\text{C}_4\text{H}_{10}$, SiH₄, Cl₂, TiCl₄ in H₂) and the deposition temperature in the range 1100–850°C. Their atomic compositions were determined by electron probe microanalysis-wave-length dispersive spectrometry (EPMA-WDS) [6].

Among them, only four samples where selected, whose atomic compositions are given in table 5. These compositions are mean values obtained from at least ten measurements performed on each sample. The overall uncertainty results from the standard errors and the counting statistic errors.

These four elemental compositions are plotted in the isothermal section of the ternary Ti–Si–C phase diagram in fig. 5, thus leading to four calculated phase compositions (table 6). These phase compositions are not very accurate and two main uncertainties may affect them to some extent. First, the Ti–Si–C phase diagram was only experimentally determined at one temperature and we implicitly assume that the isothermal section at 1100°C [9,27,28] is not fundamentally modified in the whole deposition range of temperature investigated (850–1100°C). Second, the uncertainty of the EPMA-WDS measurement could induce fundamental modifications in the phase composition. This is especially the case for coatings 1, 2 and 4 which are located near the boundary between two phase domains.

Therefore, it seemed necessary to undertake complementary characterizations. X-ray diffraction (XRD) is the easy and rapid way which is generally used to provide such information. However, while cubic SiC–orthorhombic TiSi₂ mixture could be easily identified from XRD [6], this technique was inefficient in the case of cubic SiC–cubic TiC because of the similarity of their

---

**Table 5**

Experimental atomic compositions of the codeposited samples

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>C (at%)</th>
<th>Ti (at%)</th>
<th>Si (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25±3</td>
<td>17±1</td>
<td>58±1</td>
</tr>
<tr>
<td>2</td>
<td>50±3</td>
<td>10±2</td>
<td>40±1</td>
</tr>
<tr>
<td>3</td>
<td>62±3</td>
<td>7±1</td>
<td>31±1</td>
</tr>
<tr>
<td>4</td>
<td>42±4</td>
<td>24±2</td>
<td>34±3</td>
</tr>
</tbody>
</table>

---

**Table 6**

Calculated molar compositions of the codeposited samples

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>SiC</th>
<th>TiC</th>
<th>C</th>
<th>TiSi₂</th>
<th>Ti₁SiC₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>59.5</td>
<td></td>
<td></td>
<td></td>
<td>40.5</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>17</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>11.3</td>
<td>38.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>76.5</td>
<td></td>
<td></td>
<td></td>
<td>23.5</td>
</tr>
</tbody>
</table>
Auger electron spectroscopy (AES) can give valuable information on the nature of the bonds which are present in a solid material. The following AES characterizations are intended to determine the specific features of the spectra corresponding to the compounds that may be deposited in our CVD device. The comparison with the spectra recorded on our coatings should allow the definite determination of the phase composition.

3.2.1. Auger spectra recorded in the kinetic energy range: 20–540 eV

Auger spectra, recorded in the EN(E) mode for the four coatings are shown in fig. 6.

### Table 7
SiLVV peak positions and attributed bonding states for the codeposits samples

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>SiLVV peak position (eV)</th>
<th>Attributed bonding state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>88</td>
<td>Si–C + Si–Ti</td>
</tr>
<tr>
<td>2</td>
<td>87</td>
<td>Si–C</td>
</tr>
<tr>
<td>3</td>
<td>87</td>
<td>Si–C</td>
</tr>
<tr>
<td>4</td>
<td>88</td>
<td>Si–C + Si–Ti</td>
</tr>
</tbody>
</table>

### Table 8
TiLMM peak positions and attributed bonding states for the codeposits samples

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>TiLMM peak position (EN(E))</th>
<th>Attributed bonding state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>415</td>
<td>Ti–Si</td>
</tr>
<tr>
<td>2</td>
<td>415</td>
<td>Ti–Si</td>
</tr>
<tr>
<td>3</td>
<td>415</td>
<td>Ti–Si</td>
</tr>
<tr>
<td>4</td>
<td>415.5</td>
<td>Ti–Si</td>
</tr>
</tbody>
</table>

3.2.1.1. SiLVV Auger transitions. For sample 1, the SiLVV peak position at 88 eV (table 7), is located between those of SiC (87 eV) and TiSi₂ (89.5 eV) (table 1). Furthermore, since its width is intermediate between those corresponding to the SiC and TiSi₂ peaks shown in fig. 1, this sample may contain both SiC and TiSi₂ compounds.

For samples 2 and 3, a broad SiLVV transition is observed at 87 eV whose position and lineshape are similar to that obtained for pure SiC (fig. 1 and table 1).

For sample 4, the position (88 eV) of the SiLVV transition is located between the positions measured for SiC and TiSi₂.

3.2.1.2. TiLMM Auger transitions. The TiLMM peak positions are reported in table 8. Comparison of the TiLMM transitions for samples 1 and
4 (fig. 7) with the Ti LMM transitions for reference compounds (fig. 2) suggests the presence of TiSi$_2$ into sample 1 and Ti$_3$SiC$_2$ into sample 4. The smoothed Ti L$_{23}$M$_{23}$M$_{45}$ transitions for samples 1 and 4 on one hand, and for TiSi$_2$ and Ti$_3$SiC$_2$ on the other hand, which are measured in fig. 8, confirm that hypothesis. The peak shapes and positions (416.5 eV) for samples 1 and 4, appear to be very similar to the transition observed for TiSi$_2$ and Ti$_3$SiC$_2$, respectively. In the case of samples 2 and 3, we cannot conclude definitively, because their spectra present Ti LMM line shapes which do not match accurately any of those observed for the reference compounds.

### 3.2.2. Auger spectra recorded in the kinetic energy range: 1605–1625 eV

Si KL$_{23}$L$_{23}$ Auger transitions. The broad Si KL$_{23}$L$_{23}$ transition for sample 1 being located at about 1618.5 eV suggests the presence of two different Si bonds (table 10, fig. 4). In this case, the Auger transition can be fitted with two Gaussian components, after having subtracted inelastic backscattered electrons background by using the Shirley assumption (fig. 9). The distance between the two Gaussian components at 1616 and 1618 eV agrees with the presence of Si–C bonds characteristic of SiC and Ti–Si bonds typical of TiC. For sample 3, the CKVV lineshape is characteristic of the presence of “free carbon”, but the strong intensity of this peak, do not allow concluding for the presence of carbides in the codeposit. For sample 4, the sharp CKVV peak located at 269 eV, is very similar to that of compounds having C–Ti bonds: TiC, Ti$_3$SiC$_2$ and Ti$_{0.57}$Si$_{0.33}$C$_{0.1}$. Nevertheless, the line shape of the transition on the low energy side of the main peak does not clearly reveals the narrow secondary peaks which are characteristic features of C–Ti bonds (fig. 1). We think that this line shape is, in fact, characteristic of both C–Ti and C–Si bonds.

From the Auger spectra recorded in the energy range 20–540 eV, we can conclude that:

- Sample 1 contains SiC and TiSi$_2$.
- Sample 2 contains probably SiC and TiC.
- Sample 3 contains Si–C bondings and an excess carbon. The compound containing titanium is not clearly determined.
- Sample 4 contains probably SiC and Ti$_3$SiC$_2$.

### Table 9
CKVV peaks positions and attributed bonding states for the codeposit samples

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>CKVV peaks position $EN(E)$</th>
<th>Attributed bonding state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>267</td>
<td>C–Si</td>
</tr>
<tr>
<td>2</td>
<td>269.5</td>
<td>C–Ti + C–Si</td>
</tr>
<tr>
<td>3</td>
<td>267</td>
<td>C–C</td>
</tr>
<tr>
<td>4</td>
<td>269</td>
<td>C–Ti + C–Si</td>
</tr>
</tbody>
</table>

### Table 10
Si KL$_{23}$L$_{23}$ peaks positions and attributed bonding states for the codeposit samples

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Si KL$<em>{23}$L$</em>{23}$ peaks positions $EN(E)$</th>
<th>Attributed bonding states</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1618.5</td>
<td>Si–Ti</td>
</tr>
<tr>
<td>2</td>
<td>1615.5</td>
<td>Si–C</td>
</tr>
<tr>
<td>3</td>
<td>1615.5</td>
<td>Si–C</td>
</tr>
<tr>
<td>4</td>
<td>1615.5</td>
<td>Si–C + Si–Ti</td>
</tr>
</tbody>
</table>
Fig. 9. Auger SiKL\textsubscript{23} Auger transition for sample 1 fitted into two Gaussian components which can be attributed, respectively, to SiC and TiSi\textsubscript{2} bonding states contributions. The experimental spectrum was fitted after Shirley Auger loss subtraction.

cal of TiSi\textsubscript{2}, reported at 1615.5 and 1618.5 eV, respectively.

Samples 2, 3 and 4 present a SiKL\textsubscript{23} Auger transition located at 1615.5 eV (fig. 10) which is characteristic of SiC (fig. 4). However, in the case of sample 4, the high energy side of this transition suggests a low contribution of silicon bonded to titanium as it is the case in the Ti\textsubscript{3}SiC\textsubscript{2} structure [11].

Comparison of the results obtained in the low energy range and in the high energy range allow concluding that:
- SiC and TiSi\textsubscript{2} are present in the codeposit 1.
- SiC and TiC are contained in the codeposit 2.
- SiC and “free carbon” are present in the codeposit 3, associated with titanium presumably bonded to carbon like in the codeposit 2.
- SiC and Ti\textsubscript{3}SiC\textsubscript{2} are present in the codeposit 4.

These phase attributions corroborate the calculated phase compositions given in table 4.

4. Conclusions

The energy as well as the shape of the AES peaks are characteristic features of the various compounds investigated in this work and allow a complete identification of each of them. The Auger spectra obtained for the ternary compounds Ti\textsubscript{3}SiC\textsubscript{2} and Ti\textsubscript{0.57}Si\textsubscript{0.33}C\textsubscript{0.1} are especially interesting. The carbon KVV peak looks in that case like carbide bonding. This result agrees with the crystallographic structures of these phases, in which the nearest neighbours of carbon atoms are titanium atoms [10,11]. The position and line shapes observed for the TiLMV Auger transitions are also characteristic features of each reference sample containing titanium and varies from one compound to another, in agreement with the modifications of the titanium environment. These are clearly observed for the TiLMV transition in the cases of (i) TiC (titanium surrounded by carbon atoms), (ii) TiSi\textsubscript{2} (titanium surrounded by Si atoms), and (iii) Ti\textsubscript{3}SiC\textsubscript{2} (titanium surrounded by both carbon and silicon atoms).

The results have been used successfully for the identification of Si–Ti–C CVD codeposits, specially in the case of SiC–TiSi\textsubscript{2} and SiC–Ti\textsubscript{3}SiC\textsubscript{2} mixtures. They show that AES may play a key role for bulk characterisation of ceramic mixtures, in combination with sputter etching, provided the unknown spectra are carefully compared with spectra obtained from standard phases.
References