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A. Reynes, C. Dufor, P. Mazerolles, R. Morancho. PREPARATION AND CHARACTERIZATION OF Ge-Si ALLOYS CARRIED OUT BY MOCVD. Journal de Physique Colloques, 1989, 50 (C5), pp.C5-757-C5-764. 10.1051/jphyscol:1989591 . jpa-00229624

**HAL Id: jpa-00229624**

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Submitted on 4 Feb 2008

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## PREPARATION AND CHARACTERIZATION OF Ge-Si ALLOYS CARRIED OUT BY MOCVD

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**Résumé** - L'élaboration d'alliages Si-Ge par dépôt chimique en phase vapeur a été entreprise à partir de deux composés organométalliques de formule  $\text{H}_3\text{Si}-(\text{CH}_2)_2-\text{GeH}_3$  et  $\text{H}_3\text{Si}-(\text{CH}_2)_3-\text{GeH}_3$ . Le comportement thermique de ces composés est étudié par des analyses de la phase gazeuse de décomposition et du matériau solide. Les couches obtenues sont composées de silicium, de germanium et ne contiennent pas de carbone. En fonction de ces résultats et de caractérisations physico-chimiques des précurseurs et du matériau une discussion nous amène à proposer une structure du matériau.

**Abstract** - The preparation of Ge-Si alloys by chemical vapour deposition has been undertaken using two organometallic compounds,  $\text{H}_3\text{Si}-(\text{CH}_2)_2-\text{GeH}_3$  and  $\text{H}_3\text{Si}-(\text{CH}_2)_3-\text{GeH}_3$ . Their thermal behaviour was investigated by analysis of the gaseous products of decomposition and of the solid material. The thin coatings are composed of silicon, germanium and do not contain carbon. According to these results and physico-chemical characterizations of the precursors and the products, we are lead to propose a structure for the solid material.

### 1 - INTRODUCTION

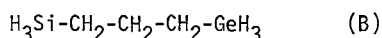
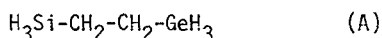
The preparation and the properties of amorphous alloys such as a  $\text{Si}_{1-x}\text{C}_x/1,2,3/$ , a  $\text{Ge}_{1-x}\text{C}_x/4/$  and a  $\text{Si}_{1-x}\text{Ge}_x/5,7,8,9/$  have been extensively studied because they present interesting semiconducting properties which are useful in solar cells or photosensors. These amorphous materials present advantages with respect to their chemical composition and structure. In particular, according to the parameter  $x$ , it is possible to vary for each kind of alloy the value of the optical gap within a relevant range. Moreover, in previous studies of these materials, various methods of preparation are used to control the  $x$  value and the structure to achieve the best properties. Two methods are : plasma assisted chemical vapour deposition, and chemical vapour deposition. In each of these methods the preparation of binary alloys is carried out using two precursors which contain the elements constitutive of the material. In the case of sputtering the precursors are solid while in Plasma Assisted Chemical Vapour Deposition (P.A.C.V.D.) and C.V.D. the precursors are gaseous. For instance in the preparation of a  $\text{Si}_{1-x}\text{Ge}_x$  alloys, the sputtering method used germanium and silicon targets/10/ and P.A.C.V.D. and C.V.D. use germane ( $\text{GeH}_4$ ) and silane ( $\text{SiH}_4$ ) as precursors.

Nevertheless, in the case of thermal C.V.D. it is not easy to control the composition  $x$  with the experimental conditions especially when the precursors have very different temperatures of decomposition. With the aim to use only one precursor which is able to carry together all the elements of the material, we have undertaken a program to study the behaviour of organometallic precursors. In preceding work /3,5/ we have already obtained  $\text{Si}_{1-x}\text{C}_x$  and  $\text{Ge}_{1-x}\text{C}_x$  alloys using organometallics. We report here the extension of this work to the elaboration of Ge-Si and Ge-Si-C alloys starting from one organometallic precursor.

## 2 - SELECTION AND SYNTHESIS OF PRECURSORS

### 2-1 - Precursor Selection

The choice of the precursors has been directed by the goal of preparing Si-Ge-C alloys whose composition is determined by the composition of the starting precursor. Two organometallic compounds (O.M.).



have been synthesized which have the following features :

- all the carbon atoms are located between the silicon and the germanium atoms.
- the number of carbon atoms is different, two atoms for the molecule A and three atoms for the molecule B.
- the bonds energies of the Si-C and Ge-C are high and quite similar ( $90 \text{ Kcal.mol}^{-1}$  for Si-C in  $\text{Si}(\text{Me})_4$  ;  $76 \text{ Kcal.mol}^{-1}$  for Ge-C in  $\text{Ge}(\text{Me})_4$ ) /11/.
- under optimal conditions of pyrolysis we anticipate the deposition of the elements in the central chains, Si-C-C-Ge and Si-C-C-C-Ge.

### 2-2 - Synthesis and characterization of the precursors

The precursors have both been synthesized according to PETROV and al. /12/. The compounds are obtained in dibutyl ether then purified by distillation. Their purity was verified by N.M.R. and Mass Spectrometry. In table I are reported the mass spectra obtained for the two molecules A and B. The fragments produced by electron impact (70 ev) display the weakness of some bonds. The most intense ions ( $I = 1000$ ) correspond to the formula  $\text{H}_3\text{Si}(\text{CH}_2)_2^+$  at  $m/e = 59$  for the molecule A and  $\text{H}_3\text{Si}(\text{CH}_2)^+$   $m/e = 45$  for the molecule B which arise from breaking of the bonds  $\alpha$  and  $\beta$  to the germanium atom. The weaker bond energy of Ge-C in Ge-CH<sub>2</sub> rather than that of Si-C in Si-CH<sub>2</sub> can explain the presence and the importance of these fragments.

| $\text{H}_3\text{Si} - \text{CH}_2 - \text{CH}_2 - \text{GeH}_3$<br>(A) |               |           | $\text{H}_3\text{Si} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{GeH}_3$<br>(B) |               |           |
|---|---------------|-----------|---|---------------|-----------|
| Principal features  | $\frac{m}{e}$ | Intensity | Principal features  | $\frac{m}{e}$ | Intensity |
| $\text{H}_3\text{Si}(\text{CH}_2)_2^+$                                  | 59            | 1000      | $\text{H}_3\text{Si}(\text{CH})_2^+$  | 45            | 1000      |
| $\text{H}_3\text{Si}^+$   | 31            | 521       | $\text{H}_3\text{Si}(\text{CH}_2)_3^+$  | 73            | 700       |
| $\text{H}_3\text{Ge}(\text{CH}_2)_2^+$                                  | 103           | 172       | $\text{H}_3\text{Ge}(\text{CH}_2)_3^+$  | 116           | 197       |
| $\text{H Ge}^+$   | 75            | 120       | $\text{H}_3\text{Ge}(\text{CH}_2)_2^+$  | 105           | 140       |

Table I : Intensities of the principal peaks coming from the mass spectra under electron bombardement at 70 ev.

### 3 - EXPERIMENTAL

The apparatus used to prepare these deposits is a cold wall reactor which has been already described elsewhere /13/. The gaseous phase coming from the decomposition enters a gas phase chromatograph for separation and analysis.

The pyrolysis of the molecules A and B have been performed at atmospheric pressure. The carrier gas was helium N55 and the total flow rate was  $10 \text{ l h}^{-1}$ . Three temperatures of decomposition were used (425, 450, 475 °C) and the temperature of the precursor source was regulated in order to have a molar fraction  $x = 10^{-3}$ .

### 4 - RESULTS

#### 4-1 - Gas phase analysis

The decomposition of each molecule as a function of the temperature of the substrate has been followed by gas chromatography. The figure 1 shows the chromatogram of gas phase of decomposition coming from the pyrolysis of molecule A. The minimum temperatures of decomposition were determined by the decrease of the chromatographic signal of the precursor or by the appearance of new signals which indicates the beginning of the decomposition /6/. These temperatures were respectively 325°C for A and 350°C for B. In the investigated range of temperatures the gases of decomposition were ethylene and acetylene for A and propene for B. Their relative presence in the gas phase is temperature dependent, the percentage of decomposition of the precursors is displayed in figure 2 for the molecules A and B.

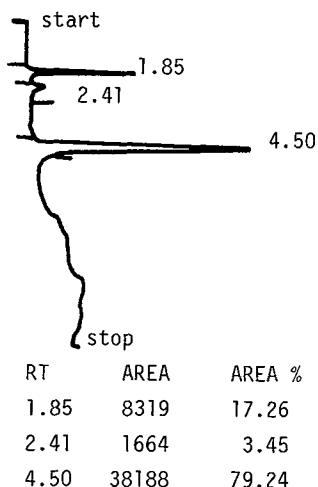


Fig. 1 : Chromatogram of molecule A.

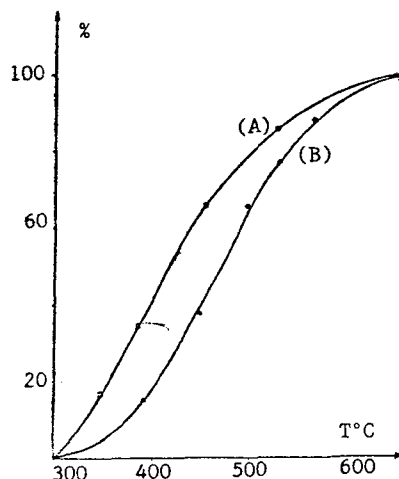


Fig. 2 : Percentage of decomposition according to the temperature.

#### 4-2 - Solid phase

The solid phase has been deposited on silica for the study of optical properties, on silicon for infrared absorption, and on alumina for analysis by energy dispersion of X Rays. In the case of thin films, the signal (Al.  $K\alpha$  line) coming from the substrate will not interact with the lines emitted by the elements of the coating.

##### 4-2-1 - Electron spectroscopy induced by X-Rays (X.P.S.)

X.P.S. analysis has been used to identify the elements included in the films and to determine by observation of chemical shifts the nature of the different bonds. The samples were examined before and after sputtering by  $Ar^+$ . The Al  $K\alpha$  monochromatized X-ray line (1486.6 eV) was used. On the surface, in addition to silicon and germanium, we note the presence of oxygen and a small peak of carbon. After ionic bombardment, the oxygen peak decreases and the carbon peak disappears. By comparison with monocrystalline germanium and silicon standard samples, we do not find any chemical shift of the germanium peaks while the silicon displays a shift towards the higher energies. Moreover the peaks 2p of the silicon are broad (width at half maximum = 3.6 eV) compared to the silicon standard sample (1.2 eV) figure (3a and 3b). This broadness may indicate that the silicon may be in different chemical forms that can be related to the presence of oxygen. On the other hand, the decrease of the oxygen intensity after sputtering shows that oxydation may occur subsequent to chemical vapor deposition reaction when the samples are in air. In any case, the most interesting feature of this study is the absence of carbon despite of the use of organometallic precursors.

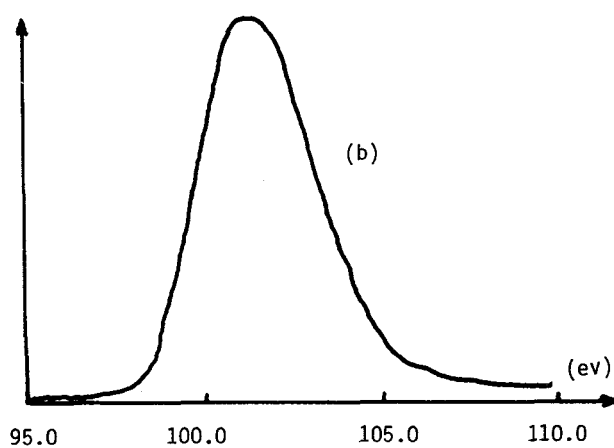
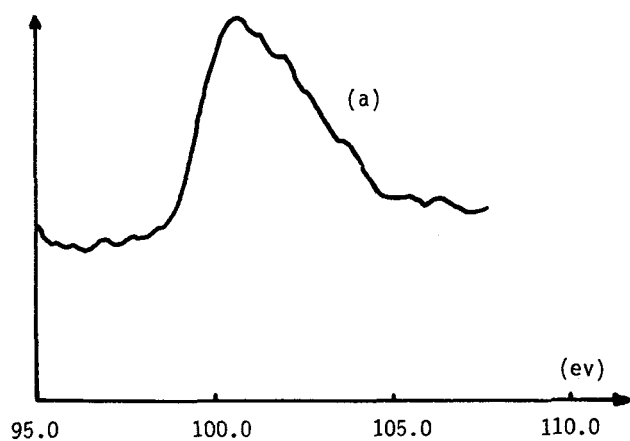


Fig. 3 : X-ray photoelectron spectroscopy of the Si<sub>2</sub>p peak in the sample carried out at 450°C from the molecule (a) in monocrystalline silicon (b).

#### 4-2-2 - Scanning electron microscopy examination and analysis by energy dispersion of X-rays

The examination of the surfaces of the samples prepared according to the experimental conditions given in table II shows ondulations arising from grains having a mean dimension of 1.4  $\mu\text{m}$  (figure 4). When the temperature of deposition increases we note a morphological evolution, the grains become smaller = 0.7  $\mu\text{m}$  at 450°C and 0.3  $\mu\text{m}$  at 500°C. A similar examination of the samples prepared from molecule B shows the same evolution. The E.D.X. quantitative analyses are displayed in table II. In the two cases (molecules A and B) the silicon percentage increases with the temperature of decomposition.

| $\text{H}_3\text{Si} - \text{CH}_2 - \text{CH}_2 - \text{Ge H}_3$ (A)               |                 |                           |                  |      |           |
|---|-----------------|---------------------------|------------------|------|-----------|
| Temperature<br>°C   | % decomposition | gases of<br>decomposition | E D A X Analysis |      | GAP<br>eV |
|   |                 |                           | % Ge             | % Si |           |
| 425   | 45              | ETHYLENE<br><br>ACETYLENE | 60               | 40   | 1.26      |
| 450   | 65              |                           | 40               | 60   | 1.02      |
| 475   | 72              |                           | 40               | 60   | 1.09      |
| $\text{H}_3\text{Si} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Ge H}_3$ (B) |                 |                           |                  |      |           |
| 425   | 27              | PROPENE                   | 50               | 50   | -         |
| 450   | 37              |                           | 40               | 60   | -         |
| 475   | 52              |                           | 30               | 70   | -         |

Table II : Principal results of the thermal decomposition of the molecules A and B.

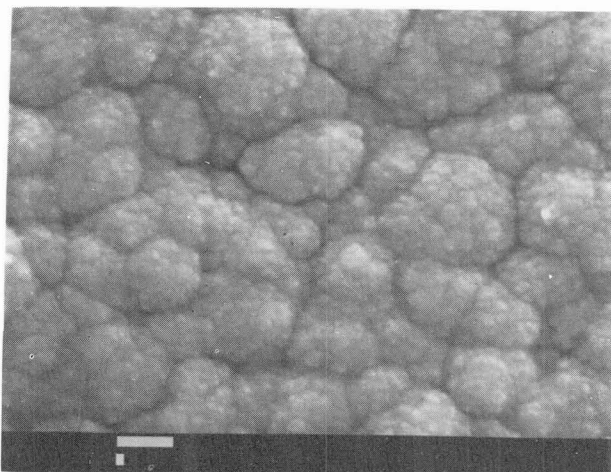


Fig. 4 : Microphotography of the surface of a sample prepared at 425°C.

#### 4-2-3 - Infrared absorption and optical gap

Infrared absorption spectra have been performed to identify possible GeH and SiH bonds whose presence would be due to the low temperature of decomposition. The results obtained with a FTIR Perkin Elmer 1710 do not show hydrogen. Meanwhile, we can see the characteristic features of a Si-O bond which is in agreement with the X.P.S. studies. The optical gaps were determined on coatings obtained from decomposition of the molecule A from the relation of MOTT and DAVIS /14/. The values reported in the table II show a weak optical gap variation as a function of the temperature of deposition and the silicon percentage.

### 5 - DISCUSSION - CONCLUSION

The results obtained from the mass spectrometry of precursor, the gaseous phase analysis after pyrolysis and the solid phase analysis permit us to propose a structure of the solid material and to understand its formation.

The stability of the ionic fragments identified by mass spectrometry may help to define the different steps of the decomposition process. Since the molar fraction is small ( $10^{-3}$ ) we expect that intermolecular interaction is less probable and, as a consequence, that the mechanism of pyrolysis will be intramolecular /15/. The principal ionic species identified in the mass spectra,  $\text{H}_3\text{Si}(\text{CH}_2)_2^+$  and  $\text{SiH}_3^+$ , for molecule A,  $\text{H}_3\text{Si}(\text{CH}_2)^+$ ,  $\text{H}_3\text{Si}(\text{CH}_2)_3^+$  and  $\text{SiH}_3^+$ , for molecule B, show that the C-Ge bonds are easily broken. Moreover the high intensities of the peaks  $\text{SiH}_3^+$  species in the mass spectra (50 % for the molecule A ; 42 % for the molecule B) suggest that the Si-C bond is cleaved with a high probability. The gaseous phase analysis is consistent with this conclusion since ethylene, acetylene and propene come respectively from the pyrolysis of molecule A and B. The central chain between the silicon and germanium atoms in the two molecules being eliminated we can postulate that the coating is built from two different entities which arise from the gaseous phase.

The optical gap values observed (1 eV - 1.3 eV) are in contradiction with those previously observed for different silicon-germanium alloys containing similar germanium percentages, obtained by sputtering or P.A.C.V.D. generally the optical gaps of such materials increase as a function of the percentage of silicon in the solid. In our case, we observe a variation in the opposite direction. This observation leads us to think that the material deposited from the A and B molecules could be heterogeneous and could be due to the presence of Ge clusters and Si clusters. As a consequence in the absorption spectra recorded to determine the optical gaps, the germanium absorbs at low frequencies while silicon absorbs at high frequencies. According to this process, the absorption spectra displays preferentially the optical absorption of germanium.

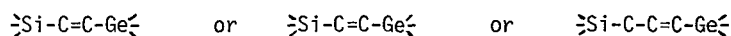
From these preliminary experiments, we can draw some conclusions :

i - the goal displayed at the beginning of the paper, i.e. keep the central chain of the molecules  $\text{SiC}_2\text{Ge}$  and  $\text{SiC}_3\text{Ge}$  has not been attained.

ii - a proposal regarding the nature of the solid product is made from the analysis of the gaseous phase of decomposition and of the solid phase.



iii - after these results on the study of heterodinuclear organometallic compounds it would be useful to modify the strength of the bonds between the metallic atoms and the bridging entities. For example, in our case, a strengthening of the Ge-C and Si-C bonds seems desirable. Actually, our work is oriented towards the synthesis of molecules presenting the following structures :



in which the double or triple bonds may have a stabilizing effect on the metal-carbon bonds by an electron transfert of the  $\pi$  electron of the multiple bond to the d orbitals of the metal atoms /16/.

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