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► **To cite this version:**

M'B. Amjoud, A. Reynes, R. Morancho, P. Mazerolles, Robert Carles. COMPARATIVE STUDY OF G_xC_x-1 FILMS PREPARED BY MOCVD FROM TETRAETHYLGERMANIUM AND TETRAVINYLGERMANIUM. Journal de Physique IV Proceedings, 1991, 02 (C2), pp.C2-327-C2-334. 10.1051/jp4:1991240 . jpa-00249830

HAL Id: jpa-00249830

<https://hal.science/jpa-00249830>

Submitted on 4 Feb 2008

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COMPARATIVE STUDY OF $\text{Ge}_x\text{C}_{x-1}$ FILMS PREPARED BY MOCVD FROM TETRAETHYLGERMANIUM AND TETRAVINYLGERMANIUM

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Abstract - The coatings coming from the thermal decomposition of two organogermanium compounds GeR_4 where R is either C_2H_5 or $\text{CH}=\text{CH}_2$ have been investigated by various technics. According to the starting molecule and the experimental conditions, the films display different features. For example the pyrolysis of $\text{Ge}(\text{CH}=\text{CH}_2)_4$ leads to the formation of a Ge-C, C-C and Ge-Ge bonds while the pyrolysis of $\text{Ge}(\text{C}_2\text{H}_5)_4$ gives Ge-Ge and few C-C bonds.

1.- Introduction.

The interest in materials prepared from elements of the fourteenth column of the periodic table is well known and their field of applications is numerous. Among the techniques used to obtain thin films, chemical vapour deposition from organometallic compounds decomposition (O.M.C.V.D.) is one of the most versatile. Moreover to obtain a given material several chemical systems can be used. For example the preparation of thin films of amorphous $\text{Si}_x\text{C}_{1-x}$ alloys is carried out from various organometallic compounds (1) such as tetraethynylsilane : $\text{Si}(\text{C}\equiv\text{CH})_4$ or tetrapropargyl silane $\text{Si}(\text{CH}_2\text{-C}\equiv\text{CH})_4$. The value of the composition x varies according to the type of the starting molecule, and particularly on the position of the triple bonds : $x = 0.82$ for the first molecule whereas $x = 0.24$ for the second. Indeed the nature of the material deposited depends on the mechanisms of pyrolysis and on the kinetics of the deposition. In order to improve our knowledge of the thermal behaviour of some organometallic precursors and try to find general rules of decomposition as a function of the radicals bonded to a metal M (Ge, Si, Sn) we have undertaken a study of the pyrolysis of organosilicon, organogermanium and organotin compounds MR_4 , MR'_2 where R is $\cdot\text{C}_2\text{H}_5$ or $\cdot\text{CH}=\text{CH}_2$, and R' is $\cdot\text{CH}=\text{CH-CH}=\text{CH}\cdot$.

In all of the molecules the ratio C/M is 8, and only the structure of the radical change. This general work concerns the studies of the mechanisms of decomposition and the analytical and structural investigations of the materials deposited as a function of the precursors. The results presented in this paper only concerns the study of the films prepared by decomposition of tetraethylgermanium $\text{Ge}(\text{C}_2\text{H}_5)_4$ (TEGe) and tetravinylgermanium $\text{Ge}(\text{CH}=\text{CH})_4$ (TVGe).

2.- Experimental details and growth kinetics.

The decomposition of the two precursors TEGe and TVGe have been carried-out in a classical horizontal hot wall reactor which has been described elsewhere (2). The experimental conditions used were the following :

- temperature of decomposition : 480-580 °C
- carrier gas flow rate : 10 l/h (He or H₂)
- mole fraction 10⁻³
- total pressure 760 torrs

Various substrates have been chosen according to the physico-chemical technique used to characterize the films : intrinsic (111) silicon and silica (puropsil) SiO₂ for Infra-Red investigations and for absorption in the UV, Visible, near Infra-Red regions respectively. For Raman and X-Ray Photoelectron Spectroscopies, either silicon or silica were used.

The thicknesses of the films prepared on silica were measured by means of a "Talystep" after etching of the material by a 10 % HF-90 % HNO₃ solution. The values found are in the range : 0,8 μm - 3,5 μm. The variation of the growth rate as a function of the temperature are shown in the Arrhenius plot in figure 1 for TEGe decomposition and in figure 2 for TVGe. Two remarks are relevant :

- i - the growth rate from TVGe is higher than from TEGe in the temperature range investigated
- ii - for the two molecules, the growth rate is favoured by the use of hydrogen as carrier-gas.

The apparent energies of activation are given in Table I for each reaction.

Table-1 The apparent energies of activation(Kcal/mole) of tow precursors. * Ref/ 3 /

Precursors Carrier gas	TEGe	TVGe
	He	34 31.3*
H ₂	41	28

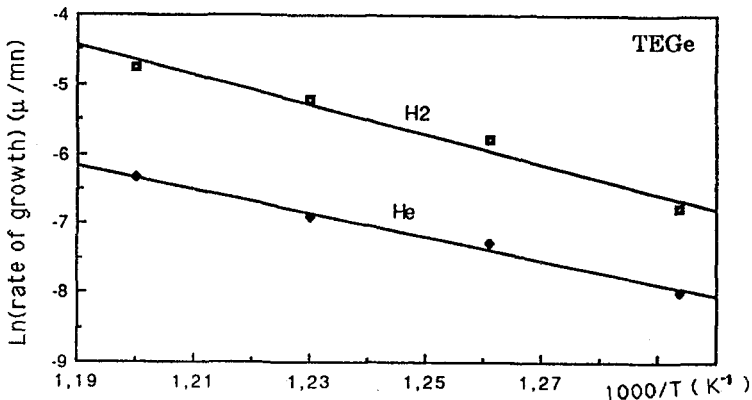


Fig.1. The growth rate of Ge_xC_{1-x} from TEGe pyrolysis in Arrhenius plot

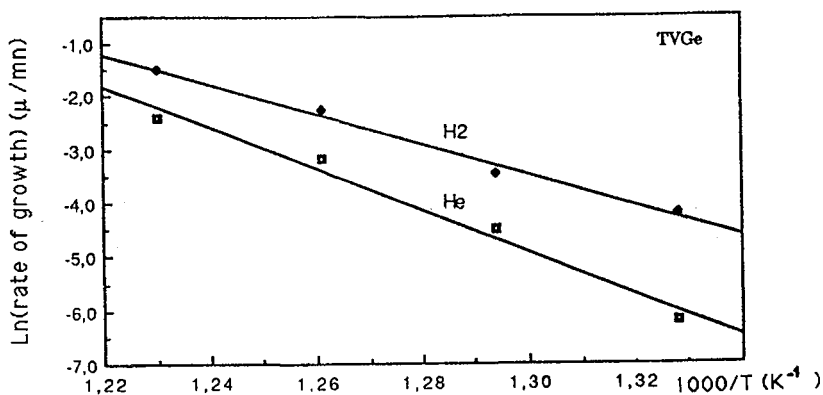


Fig.2. The growth rate of $\text{Ge}_x\text{C}_{1-x}$ from TVGe pyrolysis in Arrhenius plot.

3.- Structural studies of the films.

The structural characterization of the films has been performed by Infra-Red absorption (I.R.), X-ray Photoelectron Spectroscopy (X.P.S.) and Raman-Spectroscopy (R.S.).

3.-1 Infra-Red absorption.

The IR spectra of a film deposited at 560°C on intrinsic silicon substrates from TEGe thermal pyrolysis exhibits a wide band of weak intensity at around 1400 cm^{-1} . This feature is attributed to the stretching vibration $\nu\text{ C-C}$. On the other hand in the same range of temperature the films prepared from TVGe display the two characteristic peaks of graphitic carbon (1380 cm^{-1} and 1570 cm^{-1}). Moreover the IR spectra of these films present a strong band centered at 775 cm^{-1} (figure 3) which can be due either to the stretching of the Ge-C bond (4,5,6) or to the GeO bond (7,8). In order to assign this band we have recorded the IR spectrum of an oxidized intrinsic germanium sample (30 min at 500°C under O_2). This spectrum (figure 4) shows a strong absorption band at 875 cm^{-1} due to the Ge-O bonds. Consequently the peak located at 775 cm^{-1} in our solid phase comes from the presence of Ge-C bonds. However, the presence of a shoulder towards higher energies is indicative of partial oxidization of the films.

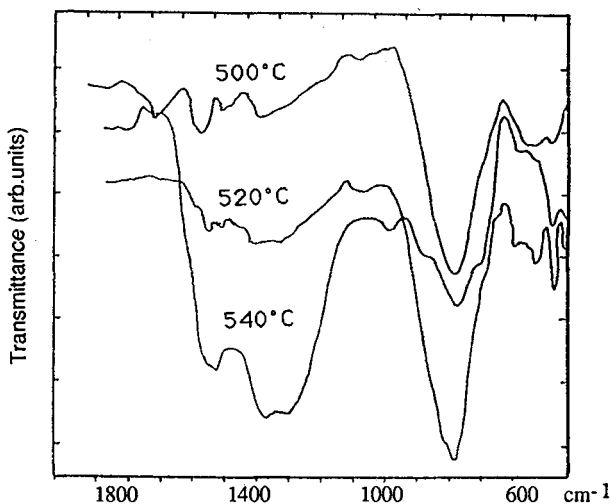


Fig. 3. I.R. absorption spectra of $\text{Ge}_x\text{C}_{1-x}$ at different temperatures of substrates from TVGe pyrolysis.

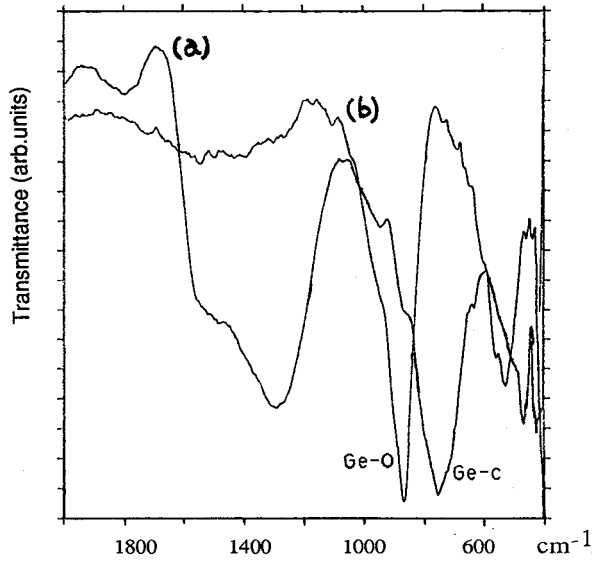


Fig.4. I R. absorption spectra of films: a) $\text{Ge}_x\text{C}_{1-x}$ prepared at 500°C under He from TVGe pyrolysis ; b) Intrinsic Ge oxidized at 500°C under O_2

3.-2 X-Ray Photoelectron Spectroscopy.

X.P.S. spectra were recorded using monochromatic $\text{Al K}\alpha_{1,2}$ radiation (1486.6 eV) after removing the contamination layer by Ar^+ ion bombardment ($E = 6 \text{ Kv}$, 100 mA, during 20 min). The energy of the gold $4f_{7/2}$ level (84 eV) has been taken as reference. A typical spectrum of a sample obtained at 500°C from TVGe pyrolysis with He carrier gas is presented in figure 5. It reveals the presence of carbon, germanium and oxygen.

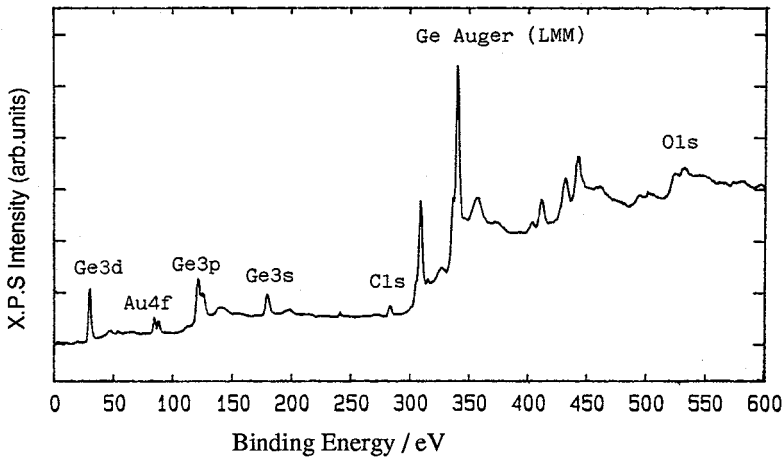


Fig.5. General XPS spectra of a coating obtained at 500°C under He from TVGe.

The X.P.S. spectra of coatings obtained from TVGe decomposition display two peaks of C 1s (figure 6a) evidencing two kinds of environments : the peak located at 284.8 eV is characteristic of C-C bonds, and we assign the peak at 283.8 eV to C-Ge bonds. This last point is conformed by the presence of Ge-C bonds revealed by the IR studies. Nevertheless the chemical shift of the Ge 3d band pointed out in figure 7 between pure standard Ge (figure 7a) and the films prepared by thermal decomposition under H₂ or He (figure 7b and 7c respectively) is not significant to explain the chemical surrounding of Ge. As a matter of fact the variation of the Fermi level in the gap of Ge as a function of the doping level may be an explanation of these small shifts. The X.P.S. spectra of the C 1s level recorded from the coatings prepared by TEGe decomposition only display one band centered at 284.5 eV. This feature is assigned to free carbon.

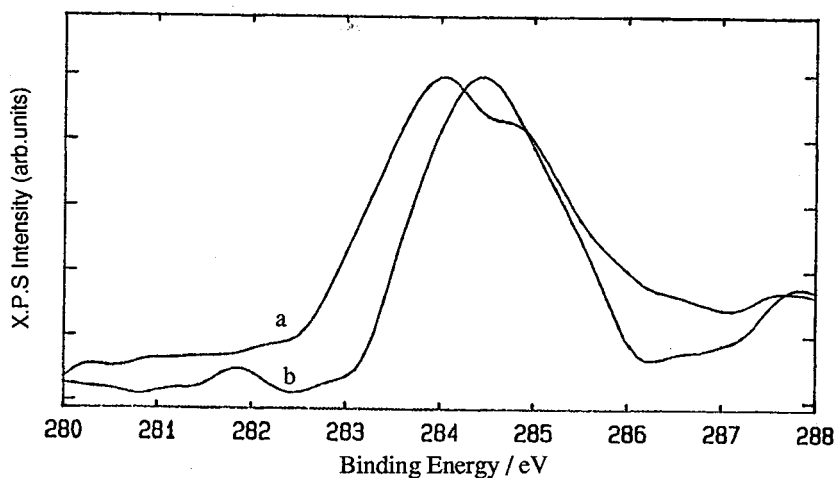


Fig.6. Binding energy of the C1s levels.Coating prepared at 500°C by pyrolysis of TVGe (a) and TEGe (b).

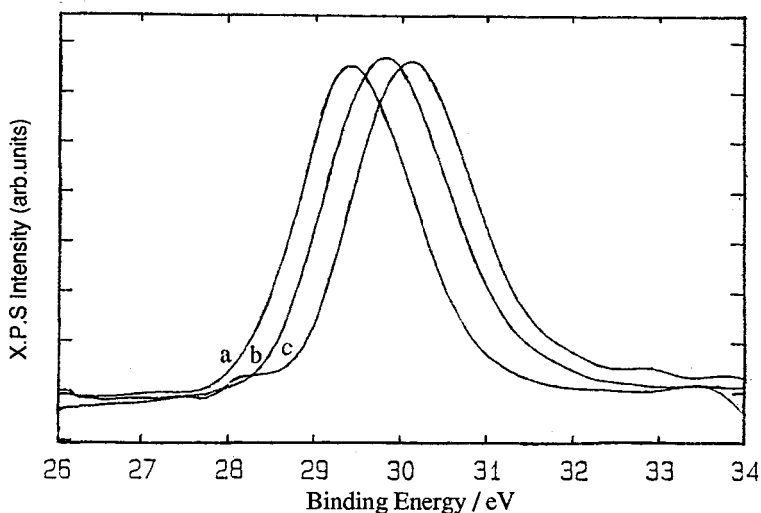


Fig.7. Binding energy of the Ge 3d levels (a) standard sample (b) coating prepared from TVGe pyrolysis at 500°C,(c) 520°C .

3.3 Raman Spectroscopy

In order to determine the crystalline quality of the films and to get further information on the local arrangements, we have performed Raman measurements. The spectra were recorded at room temperature using a grazing incidence, with the 488 nm line of an Ar laser as excitation. The signal was dispersed through a triple monochromator coupled to a conventional photon counting system. Typical spectra corresponding to the two types of precursors TVGe and TEGe, are reported in figures 8 and 9 respectively. Due to the low scattering efficiency of C-Ge bonds, we have only displayed the Ge-Ge ($250\text{-}310\text{ cm}^{-1}$) and the C-C ($1200\text{-}1700\text{ cm}^{-1}$) optical bands. No influence of the nature of the substrate was detected. The Ge-Ge bond signature consists of a single band located around 300 cm^{-1} . In the case of TVGe/He it evolves from a broad band centered at 275 cm^{-1} (figure 8a) into an asymmetrical and narrower one at 295 cm^{-1} (figure 8b), by increasing the deposition temperature. Changing the nature of the gas (He by H_2) amplifies this evolution (figure 8c and 8d). At the highest temperature the spectrum exhibits a sharp and asymmetrical peak at 301.5 cm^{-1} which coincides with the long wavelength optical mode O (Γ) of crystalline Ge. Such an evolution (a \rightarrow d) is characteristic of the enlarging of the size of crystallites in polycrystalline materials. From measurements of the full width at half maximum, one can deduce an average "Raman size" of the microcrystals. Whereas this size is less than few tenths \AA in (a), it exceeds several hundreds \AA in (d) (13). When TEGe is used (figure 9) whatever the growth conditions the crystalline nature of the Ge phase is more pronounced. In particular, at low temperature and using He (figure 9a), the amorphous like shape of the spectra (figure 9b) has disappeared. The signature of C-C, sp^2 bonding (graphitic) consist of the two bands located at 1375 cm^{-1} and 1580 cm^{-1} . The data reported in figure 8 and 9 show clearly that : (i) they are present when He is used as gas (a and b) ; (ii) their intensities rapidly decrease when the deposition temperature increases (a to b) ; (iii) the presence of a crystalline phase is favoured by the use of TVGe.

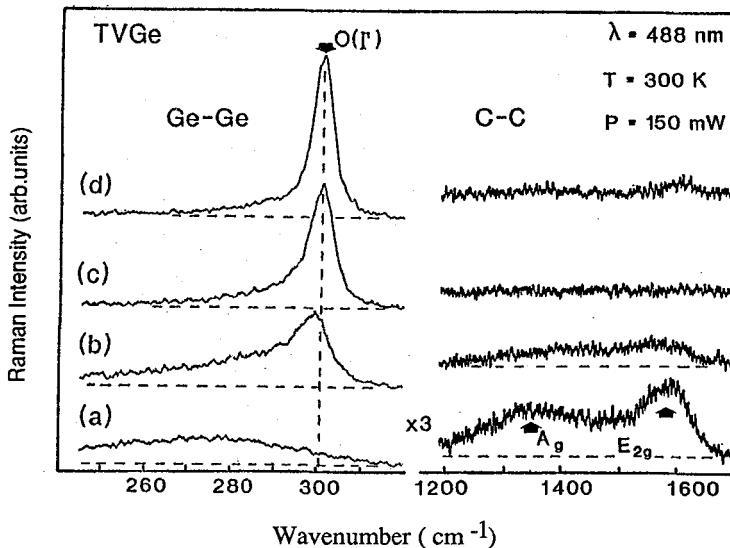


Fig.8. Typical Raman spectra of films grown using TVGe as precursor, He (a,b) or H_2 (c,d) as gas at 500°C (a,c) and 540°C (b,d).

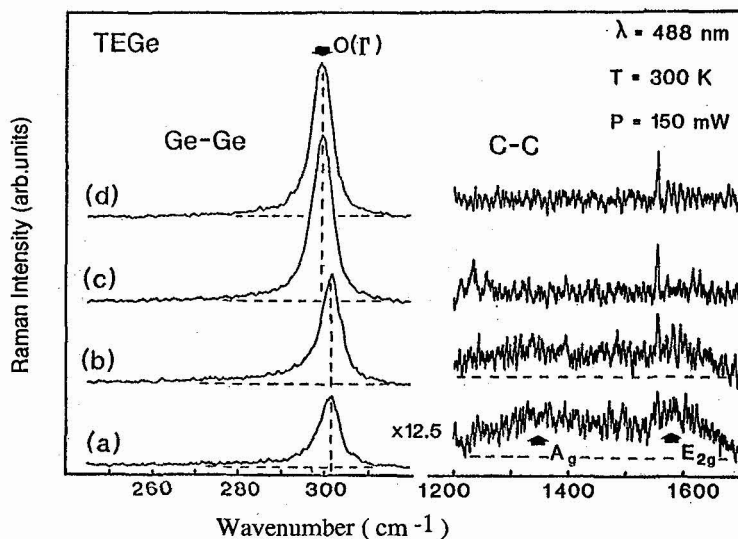


Fig.9. Typical Raman of films grown using TEGe as precursor, He (a,b) or H₂ (c,d) as gas at 500°C (a,c) and 540°C (b,d).

4.- Conclusion.

The thermal decomposition of TEGe and TVGe lead to the formation of thin Ge_xC_{1-x} films.

By using different techniques of investigations (XPS, RS and IR) there is evidence for the presence of three kinds of bonds C-C, Ge-Ge and Ge-C. In particular, Ge-C bonds have been revealed by IR spectroscopy. The carbon is present under a graphitic like phase with poor crystallization and whatever the precursor used it appears in the films at low temperature of decomposition and under He carrier gas.

At the same time, we observed an evolution of the crystallinity of the germanium phase in which grain sizes increase when the temperature goes up and when H₂ is used as carried gas. The diminution of the presence of C and the crystallinity of Ge is more readily achieved with TEGe than with TVGe.

From these first results, it appears that the behaviour of precursors having identical C/Ge ratios are not the same. In particular, the materials obtained exhibit notable microstructural differences. However in order to complete this investigation, quantitative analysis Ge and C is necessary as well as a correlation with the gas phase decomposition and this will be investigated elsewhere.

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