Characterisation and Properties of Amorphous Nonstoichiometric $Ge_{1-x}C_x$:H Compounds Obtained from X-Ray Radiolysis of Germane/Ethylene Mixtures

Paola Benzi,*[a] Mario Castiglioni,[a] and Paolo Volpe[b]

Compounds of amorphous hydrogenated nonstoichiometric germanium carbide were obtained from the radiolysis of GeH_4/C_2H_4 mixtures containing 3–30% ethylene. The composition of the materials varied depending on the ethylene percentage in the irradiated mixture. The bonding and the structure of the compounds so obtained were investigated by infrared spectroscopy, and their optical gap values determined by the Tauc procedure. The variation of optical gap values as a function of carbon content is discussed.

Introduction

In the past two decades, there has been a growth in interest in amorphous alloys (i.e. SiC, SiGe, GeC) due to their possible electronic and photovoltaic applications. A variety of different techniques are used to obtain these materials, some of which involve the decomposition of gaseous reactants.[1−9] Heat or electromagnetic quanta can provide the energy for the decomposition of the reactants. In particular, the use of high-energy quanta (i.e. X or γ) allows one to overcome the problem related with the differential activation of compounds having very different bond energies.

In our laboratory, high-energy radiation has been used to decompose gaseous mixtures with the aim of obtaining amorphous materials, particularly α-GeC:H. In fact, although the properties of germanium carbide are not well known, probably due to a lack of a simple preparation method, the theoretical conversion-yield values obtained from the plot proposed by Prince[10] using the optical gaps calculated from the Davis and Mott equation[11] suggest that the amorphous Ge−C alloys can have good photovoltaic properties depending on the Ge/C ratio.[12]

In previous work, the solids obtained from the radiolysis of mixtures of GeH_4 and saturated hydrocarbons have been studied,[15−18] but the carbon content of the solid is generally low, even when a mixture that is rich in hydrocarbons is used.

The materials prepared from mixtures of GeH_4 and unsaturated hydrocarbons are now under examination, with the aim of increasing the carbon content. In fact, mass spectrometry studies[13,14] have also suggested that the presence of the more reactive unsaturated bond can lead to an increase of carbon content in the solid. In this work we report on the characterisation of materials obtained by radiolysis of GeH_4/C_2H_4 mixtures at room temperature.

Results and Discussion

From the irradiation of germane/ethylene mixtures both volatile and condensed products are obtained, which were analysed using different techniques. The analysis of the residual gas phase (after irradiation) was performed by gas chromatography/mass spectrometry: besides unchanged ethylene and germane, di- and trigermane were revealed; traces of volatile hydrocarbons formed by condensation of two or three ethylene molecules were seldom observed. Several more interesting mixed compounds, containing from one to three germanium atoms and from one to six carbon atoms, were also detected.

In Figure 1 (**a**, **b**) variations in yields of gaseous products as a function of the ethylene percentage in the reaction mixture are shown.

The liquid or solid products obtained from radiolysis were deposited on the bottom of the irradiated vials. The colour, consistency, and physical state of these compounds depend on the ethylene percentage in the mixtures. A brown-orange dusty solid is obtained from the mixture containing 3% ethylene. If the ethylene percentage is increased the solid becomes clearer, and at around 15% ethylene content it becomes waxy. When the ethylene percentage exceeds 15% an orange liquid is formed, but when the ethylene amount reaches 30% the liquid becomes colourless.

In Table 1 the quantity, the average empirical formula and other properties of the condensed phases obtained from irradiation of germane/ethylene mixtures with ethylene ranging from 3 to 30% are reported.

The presence of hydrocarbons in the condensed phase has been excluded by solvent extraction of the products followed by gas chromatography/mass spectrometry analysis. This result is in agreement with the finding of only trace amounts of gaseous hydrocarbons in the residual gas mixture after irradiation. Moreover, the prevailing presence of

[a] Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino,
C.so Massimo D'Azeglio, 48 10125 Torino, Italy
[b] Istituto Nazionale di Fisica della Materia
E-mail address: benzi@silver.ch.unito.it

Figure 2. Ge/C atomic ratio in the condensed products obtained from irradiation as a function of Ge/C atomic ratio in the reacting gas mixture (the solid line are to guide the eye)
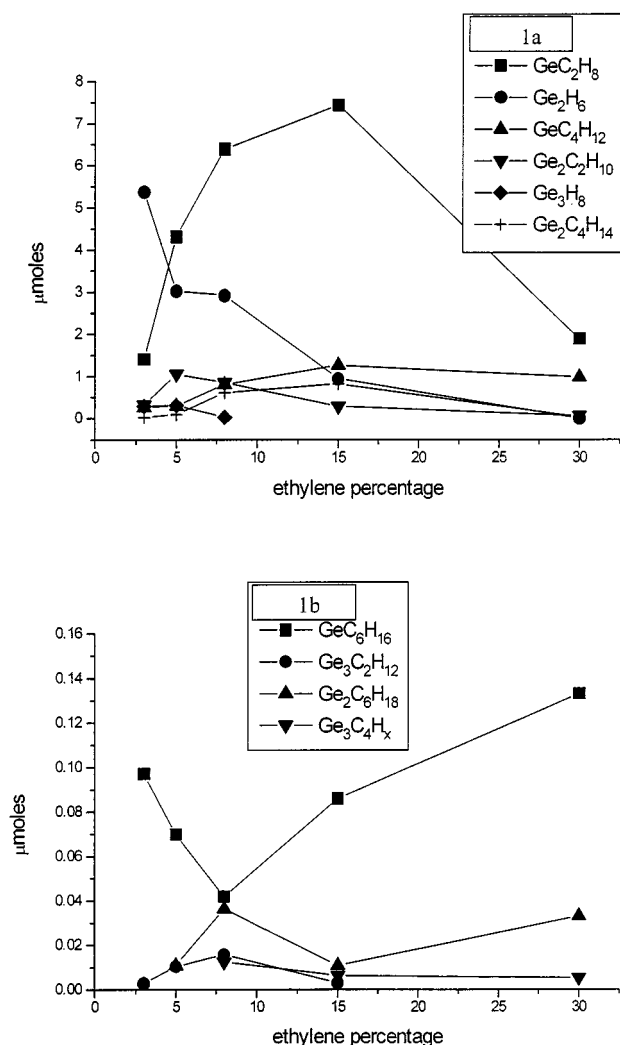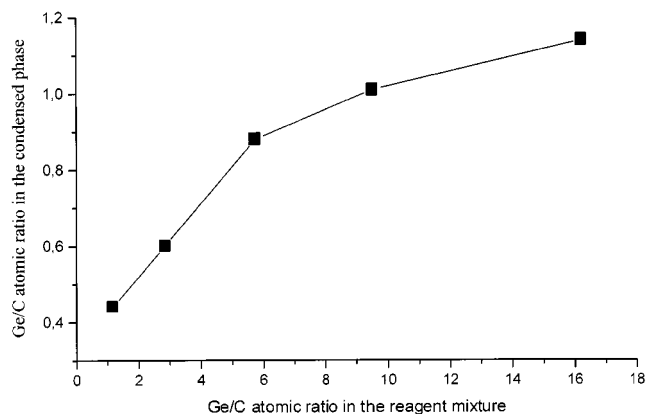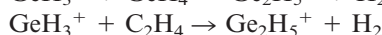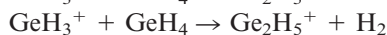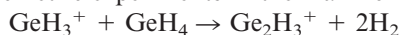
Figure 1. Gaseous products yield obtained after irradiation of germane/ethylene mixtures with different composition as a function of the ethylene percentage in the reaction mixture (the solid lines are to guide the eye); the adsorbed energy is the same for all the mixtures; NB the μmol values are affected by an error of 20%

species containing both germanium and carbon in the gas phase and the results of elemental analysis suggest that the materials obtained from irradiation of GeH_4/C_2H_4 consist of polymeric chains containing Ge−C bonds. The X-ray diffraction spectra of the compounds do not show any crystallinity i.e. the materials are in the amorphous state.

All the species formed from the various mixtures are insoluble in common organic and inorganic solvents, but are

rapidly oxidised by strong oxidising agents (such hydrogen peroxide or nitric acid). They are not very stable to the air and when exposed for a few days to the laboratory atmosphere they slowly undergo oxidation and become white. For this reason all the analyses on condensed phases were performed soon after opening the vials.

Figure 2 shows the variation of the Ge/C atomic ratio in the condensed phase obtained from irradiation as a function of the Ge/C ratio in the initial gas mixture.

As the ethylene concentration was increased in the reacting mixture, both the carbon content and the total amount of the condensed phase increased (Table 1). On the contrary, using saturated hydrocarbons,[15−18] the carbon content in the solid products increased, although the total solid yield decreased as the hydrocarbon content in the starting mixture was increased. These findings indicate that in the presence of saturated hydrocarbons, the initiation and propagation process of the polymerisation reaction leading to the solid is due to GeH_x ($n = 1-3$) species, whereas in the present experiment the ethylene molecules start and sustain the polymerisation process.

During irradiation both ionic and radical species may be involved in the formation of volatile and condensed products. From Fourier transform and high pressure mass spectrometric experiments[13] the main ionic reactions are:

$$GeH_3^+ + GeH_4 \rightarrow Ge_2H_3^+ + 2H_2$$
$$GeH_3^+ + GeH_4 \rightarrow Ge_2H_5^+ + H_2$$
$$GeH_3^+ + C_2H_4 \rightarrow Ge_2H_5^+ + H_2$$

Nevertheless, as reported in a previous paper,[19] the radical reactions should give the major contribution to the

Table 1. Composition, weight, and characteristics of the condensed products obtained from irradiation of GeH_4/C_2H_4 mixtures

| Ethylene % in the mixture | Condensed products | | $Ge_{1-x}C_x$ | % carbon[a] | % hydrogen[b] |
	Weight (mg)	characteristics			
3%	5.0 ± 0.8	brown-orange dusty solid	$Ge_{0.532}C_{0.468}$	20.6	56.0
5%	7.0 ± 1.4	dark orange dusty solid	$Ge_{0.503}C_{0.497}$	20.9	57.9
8%	10.0 ± 2.0	orange dusty solid	$Ge_{0.469}C_{0.531}$	21.4	59.5
15%	15.0 ± 1.2	orange waxy solid	$Ge_{0.376}C_{0.624}$	23.3	62.6
30%	20.0 ± 2.0	viscous colourless liquid	$Ge_{0.307}C_{0.693}$	24.6	64.5

[a] Percentage of carbon atoms in the condensed phase. − [b] Percentage of hydrogen atoms in the condensed phase.

products formation. In the same paper, from experimental data and ab initio theoretical calculations, we have hypothesised the germane radicals with one or no hydrogen atoms to be the most probable initiators of the polymeric chain:

$$GeH_n + C_2H_4 \rightarrow GeC_2H_{n+4} \quad (n = 0, 1)$$
$$GeH_n + GeH_4 \rightarrow Ge_2H_{n+4} \quad (n = 0, 1)$$

The species produced from the above reactions are still reactive and may react further with ethylene or germane molecules, leading to chain propagation up to solid products. Alternatively, they may also react with light radicals (mostly hydrogen) terminating the chain propagation and leading to volatile products.

Figure 3 shows the fraction of decomposed germane as a function of the amount of ethylene in the mixture. It increases from around 0.5 to 2% of germane when the ethylene percentage ranges from 3 to 30%.
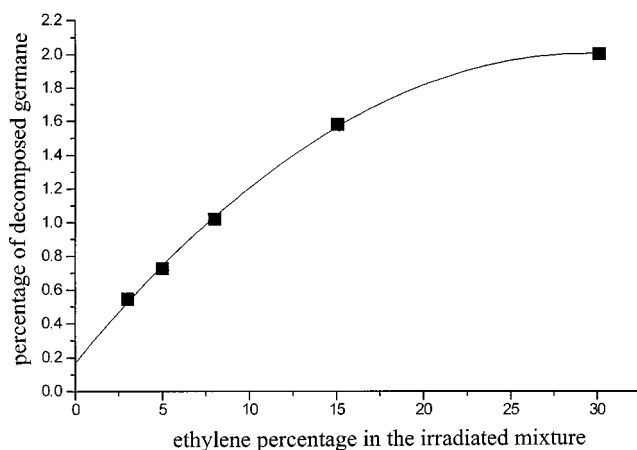

Figure 3. Percentage of decomposed germane (gaseous and condensed products are considered) with respect to the amount initially present in the mixture as a function of ethylene percentage in the irradiated mixture (the solid line is the fit of the experimental data)

This behaviour indicates that the ethylene competes effectively with hydrogen radicals in the reactions with primary and secondary radical species, promoting the chain propagation and inhibiting the radical recombination reactions. This hypothesis is also supported by the decreasing yield of di- and trigermane together with the general increase of Ge−C containing gaseous species observed when the ethylene percentage is increased. Furthermore, the ratio between the yields of condensed and gaseous products is much higher than in the GeH_4/saturated hydrocarbons system (Figure 1 and Table 1).

Bonding and Structure

IR spectroscopy was used to study the bonding configuration and structure of the α-GeC:H materials obtained. In fact the IR spectra can detect the presence and the relative abundance of CH_n, GeH_n, and GeC groups. A typical IR absorption spectrum in the 3200 to 400 cm^{-1} wave-number region, for a sample obtained from the irradiation of a 15:85 mixture of ethylene/germane, is shown in Figure 4a.
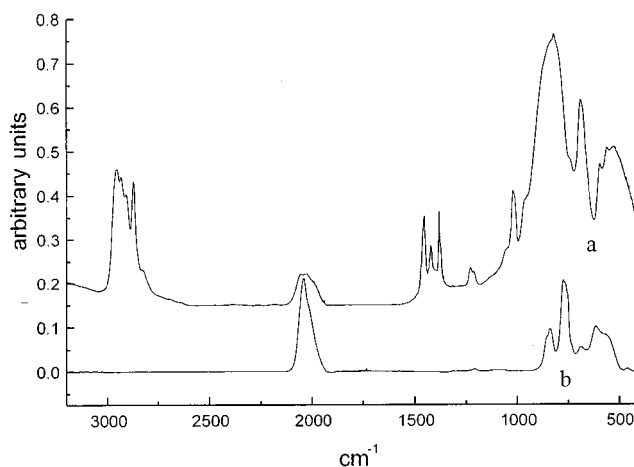

Figure 4. Infrared absorption spectrum in the 3300 to 400 cm^{-1} wave-number region of (a) a sample obtained from irradiation of the mixture with 15% ethylene, and (b) a sample obtained from irradiation of pure monogermane; the former is shifted on the y axis

In Figure 4b the spectrum of the solid obtained from irradiation of pure monogermane is shown for comparison.

The IR spectra of samples prepared from gas mixtures containing 3%, 15%, and 30% ethylene have been superimposed and divided into three regions, as depicted in Figure 5.

In the 3050 to 2800 cm^{-1} range (Figure 5a) the absorption of the CH_m ($m = 1-3$) stretching modes take place. Considering the position of the stretching bands of the CH_m ($m = 1-3$) grouping in hydrocarbons and the results reported about analogous bands in α-GeC:H and α-SiC:H,[20−24] we can assign the signals around 2955 and 2872 cm^{-1} to CH_3 groups, the signals around 2934 and 2824 cm^{-1} to CH_2 groups, and the band at 2905 cm^{-1} can be attributed to CH groups. Figure 5a shows that the intensity of the above signals increases with ethylene percentage in the reaction mixture. In particular, the normalised integrated absorption I of deconvoluted signals, defined by[21,25]

$$I = \int \alpha(\omega)\omega / d\omega$$

where α(ω) is the absorption coefficient at wave-number ω], indicates that the peak around 2955 cm^{-1}, attributed to the stretching of CH_3 groups, increases sevenfold, whereas the carbon content of the sample increases only 2.5 times (Table 1). This finding indicates that, as observed for α-SiC:H alloys,[23,24] the increase of carbon content causes the solid to incorporate a larger number of CH_3 groups. The CH_3 bonding configuration leads to a less dense material with inner surfaces or voids,[24] which allows oxygen penetration into the sample if exposed to air. This is in agreement with the above-mentioned oxidation process undergone by our samples, which becomes faster as the carbon content is higher.

Figure 5b shows the IR spectrum between 2125 and 1925 cm^{-1}. The signal is an envelope of bands whose deconvolution exhibits two partially overlapped bands at 2013 and
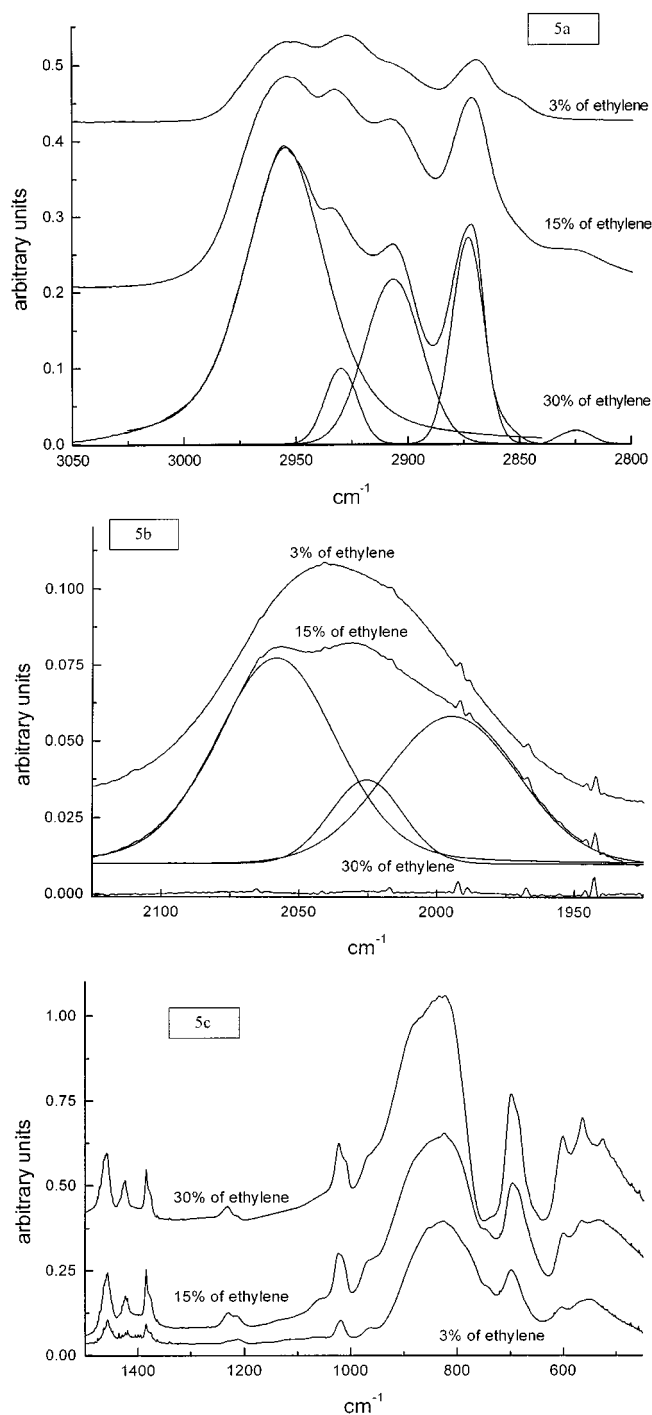
P. Benzi, M. Castiglioni, P. Volpe

Figure 5. The IR absorption bands of samples obtained from irradiation of mixtures with 3%, 15%, and 30% ethylene: **a**: (3050−2800 cm⁻¹), **b**: (2125−1925 cm⁻¹), **c**: (1500−400 cm⁻¹); in parts **a** and **b** the spectra of the samples obtained from mixtures with 3 and 15% of ethylene are shifted on the *y* axis; in part **c** the spectra of the samples obtained from mixtures with 15 and 30% ethylene are shifted on the *y* axis; the deconvoluted signals for the sample obtained from mixtures with 30 and 15% of ethylene, respectively, are also depicted in parts **a** and **b**

2051 cm⁻¹ (the deconvoluted signals are not reported in Figure 5b for clarity) and three bands at 1994, 2025, and 2058 cm⁻¹ for the samples obtained from mixtures with 3 and 15% ethylene, respectively. The sample obtained from

the mixture containing 30% ethylene does not exhibit any signals in this range. The observed bands can be assigned unambiguously to the Ge−H stretching mode, but the interpretation of the substructure of these bands involves various degrees of uncertainty.[22−28] In α-Ge:H compounds, a band at 1970 cm⁻¹ was observed and attributed both to the stretching of GeH groups inside cavities much larger than that corresponding to a monovacancy,[25,26] or to GeH₂ group stretching. Bands at 2000 and 2060 cm⁻¹ were attributed to $(GeH_2)_n$ polygermane and GeH₃ groups, respectively. On the other hand, as observed in α-SiC:H for the bands of Si−H bond stretching,[23,26] in α-GeC:H the bands due to Ge−H bond stretching can shift as the environment of the oscillatory species changes due to the presence of carbon atoms bound to germanium atoms.[21] In fact, the stretching bonds are strengthened by attaching carbon atoms to Si or Ge atoms due to the higher electronegativity of carbon with respect to Si or Ge.

In order to estimate the influence of neighbouring atoms on the frequencies of GeH and GeH₂ attached to one, two, or three carbon atoms, we have plotted, as proposed by Lukovsky for SiH and SiH₂,[29] the molecular GeH and GeH₂ vibrational frequencies (obtained from literature data[30−35]) as a function of $\Sigma SR(R_j)$, where $\Sigma SR(R_j)$ is the group-stability-ratio sum for substituting groups. The results are shown in Figures 6a and 6b.

The fits of the points give the following Equations for GeH and GeH₂ frequencies, respectively:

$$\nu(GeH) = 1740 + 27.0 \sum_{j=1}^{3} SR(Rj) \pm 13$$

$$\nu(GeH_2) = 1800 + 34.0 \sum_{j=1}^{2} SR(Rj) \pm 11$$

The frequencies for GeH and GeH₂ attached to one, two, or three carbon atoms calculated with Equation (1) and Equation (2), respectively, are summarised in Table 2.

With these indications, the band at 2013 cm⁻¹ from the sample obtained in the presence of 3% ethylene could be attributed to GeH or GeH₂ attached to two or one carbon atoms, respectively, whereas the band at 2053 cm⁻¹ could be assigned to GeH or GeH₂ bound to three or two carbon atoms, respectively. Considering the Ge/C ratio (see Table 1) we suggest that these bands are more probably due to GeH and GeH₂ modes, respectively.

Analogous considerations suggest that the three bands at 1995, 2025, and 2059 cm⁻¹ of the sample with 15% ethylene must be attributed to GeH connected to one carbon atom and to GeH₂ attached to one or two carbon atoms, respectively. However it must be considered that the band position can also be affected by the presence of internal surfaces analogously to α:Ge−H,[25,26] therefore the suggested band attribution suffers from some extent of uncertainty.

It is noteworthy that as the carbon content of the sample increases, the band's intensity in the 1950−2150 cm⁻¹ range decreases and no band is present for a sample obtained from a 30% ethylene mixture. This behaviour seems to indicate that hydrogen bound to germanium is substituted by
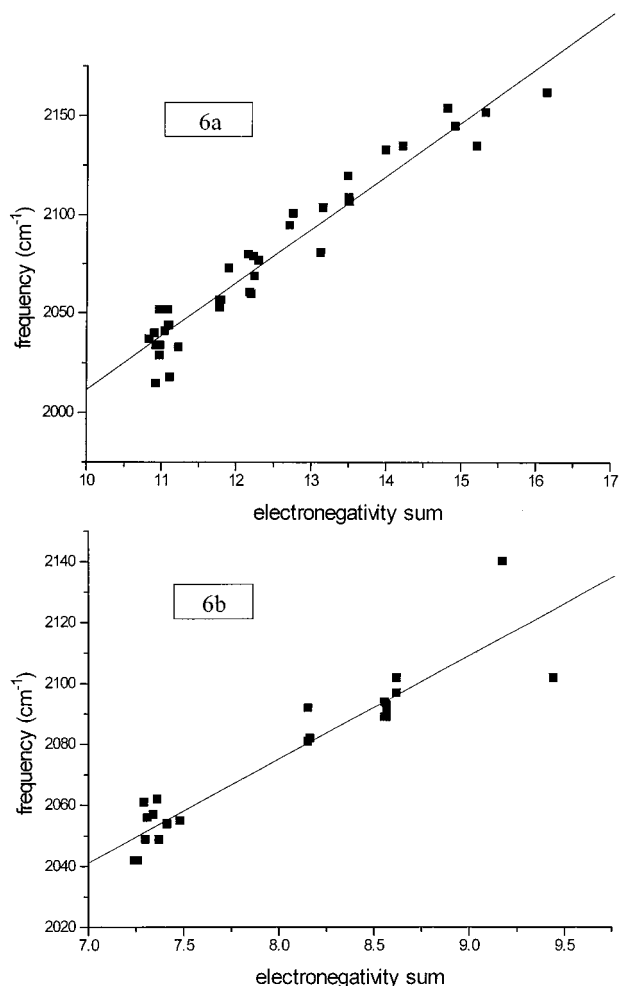
1238

Figure 6. Frequency of GeH (**a**) and GeH_2 (**b**) stretching versus electronegativity for substituted germane molecules; the points are the experimental frequencies and the solid lines are the fits to the molecular data for the di- and trisubstituted molecules

Table 2. Stretching frequencies calculated for GeH and GeH_2 groups

GeH		GeH_2	
Ge_3GeH	1952 cm^{-1}	Ge_2GeH_2	1978 cm^{-1}
Ge_2CGeH	1983 cm^{-1}	$GeCGeH_2$	2018 cm^{-1}
GeC_2GeH	2014 cm^{-1}	C_2GeH_2	2058 cm^{-1}
C_3GeH	2047 cm^{-1}		

carbon even if overall the hydrogen content in the condensed products increases. In fact, it must be considered that $E_{bond}(C-H) > E_{bond}(Ge-H)$[36] and, as observed in the α-SiC:H system,[24] the more probable bonding sites for hydrogen atoms are those having the largest bond energy. This is in agreement with both the above-mentioned increase of the band intensity attributable to CH_3 groups and the observed increase (calculated from the integral of deconvoluted signals) of the CH_3/CH_2 ratio.

Figure 5c shows the spectra in the 1500 and 400 cm^{-1} wavenumber region. In this range many bands are present,

and the interpretation is difficult due to the presence of broad bands (which are envelopes of modes) and by the overlapping of Ge−C stretching with Ge−H wagging modes or with Ge−CH_n and GeH_2 bending modes.[21,22,25] Moreover, in this region the deformation modes of $(CH_m)_nC$/Ge ($m = 1-3$; $n = 1-3$) groups are expected.[21,24]

The signals at 1385 cm^{-1} and 1458 cm^{-1} are attributable to the symmetrical and asymmetrical deformation modes of the $(CH_3)_nC$ groups ($n = 1-3$).[20,24,37] The weak band around 1424 cm^{-1}, whose intensity increases with increasing carbon and hydrogen content in the condensed phase, is probably due to the deformation mode of the CH_3Ge groups.[24,37] Two signals around 1210 and 1225 cm^{-1} are also present. Considering (i) that the intensity of the band at 1225 cm^{-1} increases while that of the band at 1210 cm^{-1} decreases with the carbon and hydrogen content, and (ii) that Rubel et al.[24] attribute the two bands around 1230 and 1245 cm^{-1} to a bending mode of $(CH_m)_nC$/Si ($m, n = 1-3$) and to a symmetric deformation mode of the CH_3Si group, respectively, the bands at 1210 and 1225 cm^{-1} have been assigned to analogous vibrational modes of CH_3Ge and $(CH_m)_nC$/Ge groups. The signal around 1024 cm^{-1} and the shoulder at 965 cm^{-1} are attributable to CH_n rocking and/or wagging modes[38,39] and to C−C stretching modes, respectively. The broad band between 950 and 750 cm^{-1} can be due to both GeH_2 and to GeH_3 bending modes and to Ge−CH_n wagging mode.[21,25] The above attribution of the signal between 2150 and 1950 cm^{-1} and the presence of a strong signal around 850 cm^{-1} for the sample from 30% ethylene (which exhibits no signal attributable to Ge−H stretching modes) support this hypothesis. The peak at 700 cm^{-1}, which exhibits an increasing intensity with ethylene percentage in the gaseous mixture, can be attributed to a rocking vibration of the CH_2 groups in the $-(CH_2)_n-$ chains with $n > 4$.[40] In the 500−650 cm^{-1} region three peaks are observed in the spectra, although other authors refer to one, two, or even four peaks, attributable both to Ge−C stretching and GeH wagging modes.[21,27,36,41] The observation of these signals even for the sample obtained from the mixture with 30% ethylene indicates that the bands between 500 and 650 cm^{-1} can be attributed to a Ge−C bond even if a contribution from the GeH group (if present) cannot be excluded.

To sum up, all the results indicate that the materials obtained from irradiation of GeH_4/C_2H_4 mixtures are amorphous nonstoichiometric $Ge_{1-x}C_x$:H compounds with chains forming a network in which the Ge atoms are less hydrogenated than the C atoms, which present many network-terminating configurations.

Optical Properties

The light absorption measurements of the samples were performed at photon energies between 0.5 and 6.25 eV. The optical gap values (E_{opt}) have been obtained from the intercept with the x axis of the extrapolated linear part of the curves calculated following the usual Tauc procedure.[42] It

consists of plotting $(\alpha h\nu)^{1/2}$ vs. the photon energy, $h\nu$, according to:

$$(\alpha h\nu)^{1/2} = B(h\nu - E_{opt})$$

where α is the absorption coefficient from spectrophotometric measurements, h Planck's constant, ν the photon frequency, B a constant, and E_{opt} the optical band gap.

The values of E_{opt} as a function of carbon molar fraction in the condensed phase are shown in Figure 7a.
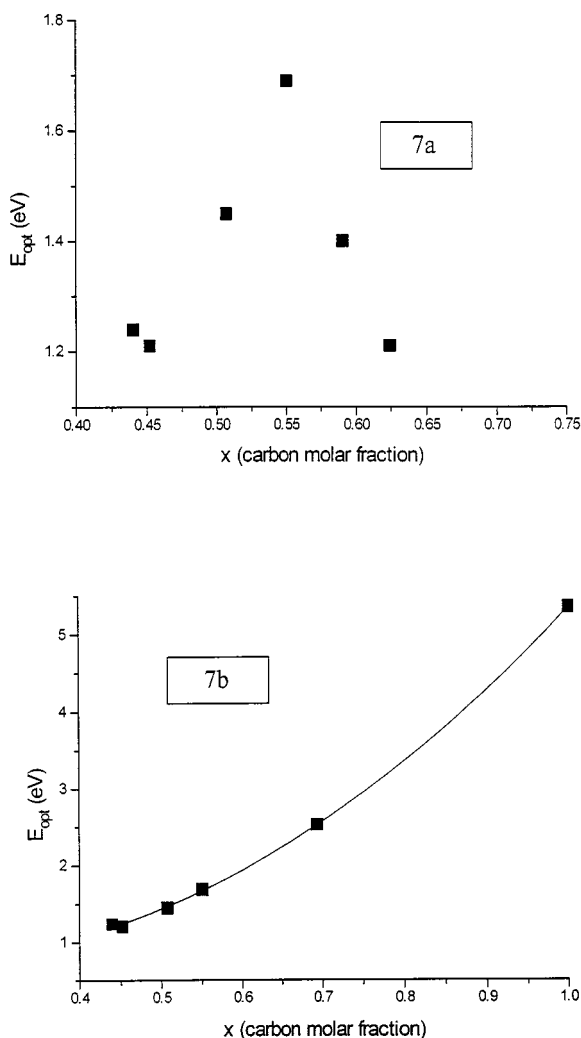

Figure 7. (a) Values of E_{opt} as a function of carbon molar fraction in the condensed phase of a few samples with different composition; (b) increasing data of part **a** and 2.53 eV are used to extrapolate to $x = 1$

The E_{opt} values are between 1.2 and 1.7 eV, which is in good agreement with previously reported data.[7,17,21,22] In particular, the sample with composition $Ge_{0.49}C_{0.51}$:H shows an E_{opt} of 1.49 eV, which is very close to the value (1.45 eV) reported by Shinar[22] for a sample with a very similar composition. Figure 7a shows that E_{opt} increases with increasing carbon content, reaching a maximum for a sample with composition $Ge_{0.45}C_{0.55}$:H, and then decreases, as reported for α-SiC:H alloys.[7] The variation of optical properties depending on film composition is related to the

local bonding. In a binary alloy, such as germanium carbide, Ge−Ge, Ge−C, and C−C bonds are possible, and their relative proportions may change with increasing carbon content. If sp^3-bonded alloys are hypothesised, E_{opt} should continuously increase with the carbon content because Ge−Ge bonds are replaced by stronger Ge−C[36] bonds. When the carbon molar fraction, x, is higher than 0.5, Ge−C bonds are replaced by even stronger C−C bonds.[36,44] Nevertheless, we observe a maximum in the plot of E_{opt} vs. carbon content at around $x = 0.55$. To explain this trend, a C sp^2-bonding configuration must be considered.[7,44,45] It is reasonable to suppose that in our Ge−C alloys with $x > 0.5$ the carbon atoms exceeding the stoichiometric composition show a tendency to form zones in which several carbon atoms are bonded together, forming a threefold coordinated graphite-type local environment, as proposed for Si−C alloys.[7] The occurrence probability of these regions is enhanced if the carbon content increases. The decrease of E_{opt} observed when the carbon content increases over a critical value both in α-GeC:H and α-SiC:H,[7,44,45] is attributed to the presence of this graphit-type carbon. This is in agreement with the approach of conduction and valence band edges shown by Robertson[44] for α-SiC:H alloys when the amount of sp^2-bonded carbon increases. Therefore, we think that the observed trend of E_{opt} for our α-Ge$_{1-x}$C$_x$:H sample, in which a maximum is present, is related to gap narrowing in carbon rich compounds due to the considerable presence of C sp^2 bonding.

An E_{opt} value of 2.53 eV has also been obtained for a sample with composition $GeC_{2.26}H_{5.92}$ (Figure 7b). This high value, which is in apparent contradiction with the above trend, is attributable to the high hydrogen content of the sample. In fact, hydrogen is found to broaden the band gap both for sp^3- and sp^2-bonded alloys.[44,45] Moreover, hydrogen promotes formation of sp^3-hybridised C atoms over sp^2, terminating any dangling bonds and thus reducing the size of the graphite-type cluster and increasing the gap. This is in agreement with the IR results that indicate that if the carbon and hydrogen content of the samples is increased, the CH$_3$-groups increase is considerably higher than the relative increase of carbon content. Moreover, it is interesting to note that if only the increasing E_{opt} values of Figure 7a and 2.53 eV are considered, the extrapolation for $x = 1$ of the line in Figure 7b, gives a value close to that of diamond (5.45 eV).[45]

Conclusions

The results obtained above indicate that amorphous non-stoichiometric Ge$_{1-x}$−C$_x$:H compounds can be obtained from X-ray radiolysis of germane/ethylene mixtures over a wide range of compositions by varying the ethylene percentage in the mixture. When the ethylene percentage is increased, the carbon and hydrogen content also increases. In the IR spectra, the vibrational modes of CH$_n$ ($n = 1−3$) and GeH$_n$ ($n = 1−2$) groups are evident. Vibrational modes of GeCH$_n$ ($n = 1−3$) groups and Ge−C bonds are also

present. The hydrogen atoms bond preferably to carbon atoms; in fact, when the carbon and hydrogen content increases the carbon hydrogenation degree increases, whereas the hydrogenation of germanium decreases indicating that the Ge−H bonds are substituted by Ge−C bonds.

The optical gaps of the compounds depend on the carbon content: values between 1.2 and 1.7 eV have been found. The E_{opt} increases with increasing carbon molar fraction until it reaches a critical value around 0.55, and then decreases giving a maximum in E_{opt}. This trend is attributed to the presence of sp^2-hybridised C atoms forming π-bonded clusters when the carbon molar fraction exceeds 0.55.

Experimental Section

Monogermane was prepared according to a literature procedure,[46] and purified by bulb-to-bulb distillation. Ethylene was high purity SIAD (Società Italiana Acetilene e Derivati) gas and was used without further purification.

Samples of GeH_4/C_2H_4 mixtures of different composition were irradiated with 250 keV X-rays in 365-mL Pyrex vessels at a total pressure of 700 Torr. During irradiation, performed under static conditions, the irradiated mixture composition did not vary markedly. Moreover, as the condensed products were deposited on the bottom of the vials, out of the main X-ray trajectory, the dose absorbed by the products was negligible.

Standard vacuum techniques were used to handle both reactants and gaseous products.

The X-ray source was a CPXT-320 tube (Gilardoni) with a maximum output of 320 keV. The dose absorbed by each sample was 5.0×10^4 Gy at a rate of 1.0×10^4 Gy/h. During the irradiation the temperature did not exceed 320 K.

Gas phase products were analysed by gas chromatography-mass spectrometry (GC-MS) on a Varian 3400-Finnigan ITD instrument equipped with an Alltech AT-1 chromatographic column (polydimethylsiloxane, length 30 m, I.D. 0.25 mm, film thickness 1.0 μm). The temperature ranged from 243 K to 523 K at 10 K/min. A He carrier head pressure of 10 psi was used. Ionisation in the trap was achieved by 70 eV EI and ion acquisition was recorded in the 20−650 u mass range. Quantitative determination of volatile compounds was accomplished calibrating the gas chromatograph with GeH_4. The values reported are the average of at least four experiments.

The composition of the solids was determined by elemental (C and H) analysis.

The X-ray powder-analyses were performed on a Siemens D 500 diffractometer, using Cu-K_α radiation (graphite monochromator on the secondary beam).

The condensed phases were examined by IR spectroscopy (KBr pellets) with an FTIR Bruker Equinox 55 instrument equipped with a program for the deconvolution of overlapped peaks. The resolution was 2 cm^{-1}. All spectra were gathered at room temperature.

The UV/Vis spectrum was obtained with a Perkin−Elmer Lambda 15 spectrophotometer from the material deposited on the quartz disk, using a clean quartz disk irradiated at the same dose as a reference.

Acknowledgments

[1] T. Drüsedau, A. Panckow, W. Herms, H. Sobotta, V. Riede, R. Böttcher, A. Witzmann, *J. Non-Cryst. Solids* **1993**, *155*, 195.

[2] C. K. Seal, D. Samara, S. K. Banerjee, *Appl. Phys. Lett.* **1997**, *71*, 3564.

[3] T. Drüsedau, B. Schröder, *Appl. Phys. Lett.* **1992**, *61*, 566.

[4] J. Tyczkowski, E. Odrobina, M. Gazicki, F. Olcaytug, *J. Non-Cryst. Solids* **1991**, *137/138*, 875.

[5] Y. Nakayama, S. Akita, M. Nakano, T. Kawamura, *J. Non-Cryst. Solids* **1987**, *97/98*, 1448.

[6] S. Z. Han, H. M. Lee, H-S Kwon, *J. Non-Cryst. Solids* **1994**, *170*, 199.

[7] N. Saito, *J. Non-Cryst. Solids* **1989**, *108*, 211.

[8] D. A. Anderson, W. E. Spear, *Phil. Mag.* **1977**, *35*, 1.

[9] Y. Tawada, K. Tsuge, M. Kondo, H. Okamoto, Y. Hamakawa, *J. Appl. Phys.* **1982**, *53*, 5273.

[10] M. Prince, *J. Appl. Phys.* **1955**, *526*, 534.

[11] E. A Davis, N. F. Mott, *Philos Mag.* **1970**, *22*, 903.

[12] P. Mazerolles, R. Morancho, A. Reynes, *Silicon, Germanium, Tin Lead Compd.* **1986**, *9*, 243.

[13] P. Benzi, P. Operti, G. A. Vaglio, P. Volpe, M. Speranza, R. Gabrielli, *J. Organometal. Chem.* **1989**, *373*, 289.

[14] P. Benzi, L. Operti, G. A. Vaglio, P. Volpe, *Int. J. Mass Spectrom. Ion Proc.* **1990**, *100*, 647.

[15] P. Antoniotti, P. Benzi, M. Castiglioni, L. Operti, P. Volpe, *Chem. Mater.* **1992**, *4*, 717.

[16] P. Benzi, M. Castiglioni, P. Volpe, *J. Mater. Chem.* **1994**, *4*, 1067.

[17] P. Benzi, M. Castiglioni, E. Truffa, P. Volpe, *J. Mater. Chem.* **1996**, *6*, 1507.

[18] P. Antoniotti, P. Benzi, M. Castiglioni, L. Operti, P. Volpe, *Radiat. Phys. Chem.* **1996**, *48*, 457.

[19] P. Antoniotti, P. Benzi, M. Castiglioni, P. Volpe, *Eur. J. Inorg. Chem.* **1999**, 323.

[20] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 3rd ed., Chapman and Hall, London, **1975**, p. 13.

[21] T. Drüsedau, A. Andreas, B. Schröder, H. Freisted, *Philos. Mag.* **1994**, *69*, 1.

[22] J. Shinar, H. S. Wu, R. Shinar, H. R. Shanks, *J. Appl. Phys.* **1987**, *62*, 808.

[23] H. Wieder, M. Cardona, C.R. Guarnieri, *Phys. Stat. Sol.* **1979**, *92*, 99.

[24] H. Rübel, B. Schröder, W. Fuhs, J. Krauskopf, T. Rupp, K.Bethge, *Phys. Stat. Sol.* **1987**, *139*, 1351.

[25] M. Cardona, *Phys. Stat. Sol.* **1983**, *118*, 463.

[26] G. Lucovsky, *J. Non-Cryst. Solids* **1985**, *76*, 173.

[27] S. Kumar, S. C. Kashyap, K. L. Chopra, *J. Non-Cryst. Solids* **1988**, *101*, 287.

[28] W. Paul, S. J. Jones, W. A. Turner, P. Wickboldt, *J. Non-Cryst. Solids* **1992**, *141*, 271.

[29] G. Lucovsky, *Solid State Commun.* **1979**, *29*, 571.

[30] R. Mathis, M. Constant, J. Satge, F. Mathis, *Spectrochim. Acta* **1964**, *20*, 515.

[31] R. Mathis, J. Satge, F. Mathis, *Spectrochim. Acta* **1962**, *18*, 1463.

[32] A. N. Egorochkin, E. I. Sevast′yanova, S. Ya. Khorshev, S. Kh. Ratushnaya, J. Satge, P. Riviere, J.Barrau, S. Richelme, *J. Organometal. Chem.* **1978**, *162*, 25.

[33] R. Eujen, R. Mellies, E. Petrauskas, *J. Organometal. Chem.* **1986**, *299*, 27.

[34] A. N. Egorochkin, S. Ya. Khorshev, E. I. Sevastyanova, S. Kh. Ratushnaya, J. Satge, P. Riviere, J. Barrau, S. Richelme, *J. Organometal. Chem.* **1978**, *155*, 175.

[35] R. Mathis, M. Barthelat, F. Mathis, *Spectrochim. Acta* **1993**, *26*, 1993.

[36] *CRC Handbook of Chemistry and Physics*, 78th ed. CRC Press, Boca Raton and New York, **1997−1998**.

[37] G. K. Barker, J. E. Drake, R. T. Hemmings, B. Rapp, *Spectrochim. Acta* **1972**, *28A*, 1113.

[38] F. Demichelis, G. Kaniadakis, A. Tagliaferro, E. Tresso, P. Rava, *Proc. Intern. PVS EC-3* **1987**, 313.

[39] A. Marchand, P. Gerval, P. Riviere, J. Satge, *J. Organometal. Chem.* **1978**, *162*, 365.

[40] B. Schrader, in *Infrared and Raman Spectroscopy*, VCH, Weinheim, **1995**, p. 192.

[41] Y. Chaterine, G. Turban, *Thin Solid Films* **1980**, *70*, 101.

[42] L. Ley, in *The Physics of Hydrogenated Amorphous Silicon II*, Springer-Verlag, Berlin **1984**, p. 142.

[43] G. A. N. Connel, J. R. Pawlik, *Phys. Rev. B* **1976**, *13*, 787.

[44] J. Robertson, *Phil. Mag.* **1992**, *66*, 615.

[45] H. Yuan, R. Williams, *Chem. Mater.* **1993**, *5*, 479.

[46] A. J. Jolly, J. E. Drake, *Inorg. Synth.* **1963**, *7*, 37.