Characterization and Properties of Amorphous Nonstoichiometric $Ge_{1-x}-C_x$:H Compounds Obtained by Radiolysis−CVD of Germane/Ethyne Systems

Paola Benzi,*,[†,‡] Elena Bottizzo,[†] Lorenza Operti,[†] and Paolo Volpe[†,‡]

Dipartimento di Chimica Generale ed Organica Applicata, Università degli Studi di Torino, Corso Massimo d'Azeglio 48, 10125 Torino, Italy, and Istituto Nazionale di Fisica della Materia, Villa Brignole, Corso Perrone, 24, 16152 Genova, Italy

Received June 27, 2003. Revised Manuscript Received December 1, 2003

Amorphous germanium carbides have been prepared by X-ray activated chemical vapor deposition from germane/ethyne systems. The materials composition is found to change depending on the ethyne percentage in the irradiated mixture. The bonding and the structure of the compounds so obtained were investigated by infrared spectroscopy and the optical gap values have been determined from UV−vis spectra. The variation of optical gap values as a function of carbon content is discussed.

Introduction

The amorphous alloys, as Si−C, Si−Ge, and Ge−C, have been grown in interest due to their possible electronic and photovoltaic applications and to their low cost compared with that of the crystalline form.[1,2] Some of the techniques used to obtain these compounds involve the decomposition of reactants in the gaseous phase.[3−13] This allows one to obtain materials with composition varying in a wide range, changing the nature and/or the concentration of the reactants. In our laboratory we use high-energy radiations (X-ray) to obtain amorphous hydrogenated nonstoichiometric germanium carbide from GeH_4/hydrocarbons mixtures. The results obtained in previous works show that if alkanes are used, the carbon content in the materials increases with the number of carbon atoms in the reactant hydrocarbon molecule but it remains low even when a high hydrocarbon molar fraction in the irradiated mixture is used. A sharp increase in the carbon content is observed when ethene is used and mass spectrometric studies[14,15] show that the chain propagation is favored by increasing insaturation of hydrocarbons.[16,17]

Therefore, we have performed the radiolysis of mixtures containing germane and ethyne with the aim of obtaining higher yields of solid material, possibly as films. Germane/ethyne mixtures have been used in different ratios and in this work we report on the characterization of materials obtained at room temperature.

Experimental Section

Monogermane was prepared as described in the literature[18] starting from GeO_2 and KBH_4; ethyne was supplied by SIAD SpA (Società Italiana Acetilene e Derivati) at 99.99% stated purity. Both gases were purified by bulb-to-bulb distillation under vacuum and dried with sodium sulfate. The GeH_4/C_2H_2 mixtures with different composition were prepared in 365-mL Pyrex vessels at a total pressure of 700 Torr (1 Torr = 133 Pa) prior to the X-ray treatment. Standard vacuum techniques were used to handle reactants and gaseous products.

Two sets of mixtures were irradiated: in the first one (series A) the bottom of the vials, where the solid products are deposited, was positioned out of the main X-ray trajectory; in the second one (series B) the bottom of the vials was on the X-ray trajectory. In fact, the different conditions of deposition can give valuable information on the mechanisms leading to the solid materials.

The X-ray source was a CPXT-320 tube (GILARDONI) with a maximum output of 320 keV X-ray. The dose absorbed by each sample was 5.0×10^4 Gy at a rate of 1.0×10^4 Gy/h. During irradiation the temperature never exceeded 320 K.

After irradiation, a small amount of the gas phase was drawn for qualitative and quantitative analyses of volatile

---

* To whom correspondence should be addressed. Fax: 39 011 670 7591. E-mail: paola.benzi@unito.it.

[†] Università degli Studi di Torino.

[‡] Istituto Nazionale di Fisica della Materia.

(1) Mazerolles, P.; Morancho, R.; Reynes, A. *Silicon, Germanium, Tin, Lead Compd.* **1986**, *9*, 243−271.

(2) Seraphin, B. O. *Optical Properties of Solids. New Developments*; North-Holland Publishing Co.: Amsterdam, The Netherlands, 1976.

(3) Drüsedau, T.; Andreas, A.; Schröder, B.; Freisted, H. *Philos. Mag.* **1994**, *69*, 1−20.

(4) Seal, C. K.; Samara, D.; Banerjee, S. K. *Appl. Phys. Lett.* **1997**, *71*, 3564−3566.

(5) Drüsedau, T.; Schröder, B. *Appl. Phys. Lett.* **1992**, *61*, 566−568.

(6) Tyczkowski, J.; Odrobina, E.; Gazicki, M.; Olcaytug, F. *J. Non-Cryst. Solids* **1991**, *137&138*, 875−878.

(7) Nakayama, Y.; Akita, S.; Nakano, M.; Kawamura, T. *J. Non-Cryst. Solids* **1987**, *97&98*, 1447−1450.

(8) Han, S. Z.; Lee, H. M.; Kwon, H.-S. *J. Non-Cryst. Solids* **1994**, *170*, 199−204.

(9) Saito, N. *J. Non-Cryst. Solids* **1989**, *108*, 211−215.

(10) Anderson, D. A.; Spear, W. E. *Philos. Mag.* **1977**, *35*, 1−16.

(11) Tawada, Y.; Tsuge, K.; Kondo, M.; Okamoto, H.; Hamakawa, Y. *J. Appl. Phys.* **1982**, *53*, 5273−5281.

(12) Wieder, H.; Cardona, M.; Guarnieri, C. R. *Phys. Status Solidi B.* **1979**, *92*, 99−112.

(13) Kumar, S.; Kashyap, S. C.; Chopra, K. L. *J. Non-Cryst. Solids* **1988**, *101*, 287.

(14) Benzi, P.; Operti, L.; Vaglio, G. A.; Volpe, P.; Speranza, M.; Gabrielli, R. *J. Organomet. Chem.* **1989**, *373*, 289−300.

(15) Benzi, P.; Operti, L.; Vaglio, G. A.; Volpe, P.; Speranza, M.; Gabrielli, R. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 647−663.

(16) Antoniotti, P.; Benzi, P.; Castiglioni, M.; Volpe, P. *Eur. J. Inorg. Chem.* **1999**, 323−332.

(17) Benzi, P.; Castiglioni, M.; Volpe, P. *Eur. J. Inorg. Chem.* **2001**, 1235−1242.

(18) Jolly, A. J.; Drake, J. E. *Inorg. Synth.* **1963**, *7*, 37.

10.1021/cm034547z CCC: $27.50

Table 1. Distribution of Gaseous Compounds (from B series) Obtained after Irradiation of Mixtures with Different Ethyne Percentage

ethyne percentage	gases[a] (mmol)				
	GeC_2H_4	GeC_2H_6	$Ge_2C_2H_6$	$Ge_2C_2H_8$	Ge_2H_6
10%		0.024	0.033	0.210	traces
20%		0.028	0.109	0.525	traces
30%		0.012	0.015	0.089	
50%	0.003	0.012	0.020	0.094	
80%	traces of hydrocarbons with 4 or 6 carbon atoms				

[a] Determinations are affected by an error within 15%.

compounds by GC/MS on a VARIAN 3400-Finnigan ITD instrument equipped with an Alltech AT-1 chromatographic column (poly(dimethylsiloxane), length 30 m, i.d. 0.25 mm, film thickness 1.0 μm).

The temperature ranged from 233 to 323 K at a rate of 10 K/min. A split of about 15 mL/min was applied during injection; He carrier pressure of 10 psi (1 psi = 6.89×10^3 Pa) was used. Ionization in the trap was achieved by 70-eV electron and ion acquisition was performed in the 50−400 u mass range.

Quantitative determination of volatile compounds was obtained by correlating the areas of the gas chromatographic peaks to the total number of millimoles of gases, determined by measuring the pressure in the reacting vessel of known volume.

The solid products were collected and weighed and their composition was determined via elemental (C and H) analysis. The density was measured with a Berman balance (vs toluene).

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

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

EPR spectra were collected on an X-band Varian 109 instrument equipped with an E232 dual-sample cavity (9.5-GHz resonant frequency).

Samples were also investigated with a scanning electron microscope (SEM) Oxford Instrument.

The UV−vis spectra were 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.

To avoid any possible oxidation by oxygen in the air, all the analyses on solids were performed soon after opening the vials.

Results and Discussion

From the irradiation of germane/ethyne mixtures, solid products are obtained, which deposited on the bottom of irradiated ampules. The analysis of the residual gas phase (after irradiation) was performed by GC-MS, and besides unreacted germane and ethyne, compounds containing both germanium and carbon were detected. Traces of digermane are also present in the irradiated mixtures with 10 or 20% of ethyne, whereas small amounts of hydrocarbons with 4 or 6 carbon atoms are detected in the irradiated mixture with a large ethyne excess (80%). At room temperature the solids are stable to the air and insoluble in the common organic solvents, but they are rapidly oxidized if heated in air or treated with oxidizing agents.

In Table 1 the typical distribution of gaseous compounds (from B series) obtained after irradiation of mixtures with different ethyne percentage is reported.

Table 2. Quantity, Average Empirical Formula, Optical Gap, and Other Characteristics of the Solids Obtained from Irradiation of Germane/Ethyne Mixtures

ethyne percentage in the mixture	condensed products from A series mixtures		
	weight[a] (mg)	characteristics	empirical formula
5%		dark orange solid	$GeC_{1.03}H_{3.27}$
10%	38	dark orange solid	$GeC_{1.76}H_{4.49}$
20%	72	orange solid	$GeC_{1.98}H_{4.63}$
30%	118	yellow solid	$GeC_{2.83}H_{5.77}$

ethyne percentage in the mixture	condensed products from B series mixtures			
	weight[a] (mg)	characteristics	empirical formula	optical gap
10%	43	dark orange solid	$GeC_{1.56}H_{4.08}$	0.26
20%	107	orange solid	$GeC_{1.93}H_{4.63}$	0.05
30%	193	yellow solid	$GeC_{2.46}H_{5.77}$	1.61
50%	322	white solid	$GeC_{2.94}H_{6.32}$	2.41

[a] Determinations are affected by an error within 10%.

From this table it is worth noting that only GeC_2H_6, $Ge_2C_2H_6$, and $Ge_2C_2H_8$ are always present after irradiation of the GeH_4/C_2H_2 mixtures, whereas several gaseous species containing both carbon and germanium were detected after radiolysis of the GeH_4/C_2H_4 mixtures.[17] This behavior is in agreement with the literature data on ethene and ethyne radiolysis, giving several gaseous compounds from ethene, but only benzene from ethyne. Among the GeH_4/C_2H_2 products $Ge_2C_2H_8$ has the highest yield and it is 5−6 times more abundant than $Ge_2C_2H_6$. Data reported in Table 1 indicate that the self-condensation reaction of germane or ethyne are negligible with respect to reactions which lead to species containing both germanium and carbon atoms.

In fact, digermane is only detected when germane in the reacting mixture is higher than 80% and pure hydrocarbons are found only in mixtures with a large excess of ethyne (80%).

In Table 2 the quantity, the average empirical formula, and other characteristics of the solid phases obtained from irradiation of germane/ethyne mixtures are reported.

Ethyne ranges from 5 to 30% and from 10 to 50% for samples of series A and series B, respectively.

It is noteworthy to remind that previously performed experiments on germane alone[19,20] produced a black powder of an amorphous cross-linked polymer and di- and trigermane in the gas phase. Moreover, at the total dose used here, no solid product is formed from irradiation of ethyne alone and only hydrocarbons with 4 or 6 carbon atoms are observed in the gas phase. All these results indicate that the solids collected are not simple coprecipitation of hydrogenated C−C or Ge−Ge polymer chains, but do contain Ge−C bonds. The color of the solid products changes with ethyne percentage in the irradiated mixture: a dark orange solid is obtained from mixtures with 10% of ethyne, becoming more clear with increasing percentage of ethyne; the solid obtained from the 50% mixture is white. Results in Table 2 show that

---

(19) Belluati, R.; Castiglioni, M.; Volpe, P.; Gennaro, M. C. *Polyhedron* **1987**, *6*, 441.

(20) Battezzati, L.; Benzi, P.; Castiglioni, M.; Venturi, M.; Volpe P. *Polyhedron* **1988**, *7*, 597.

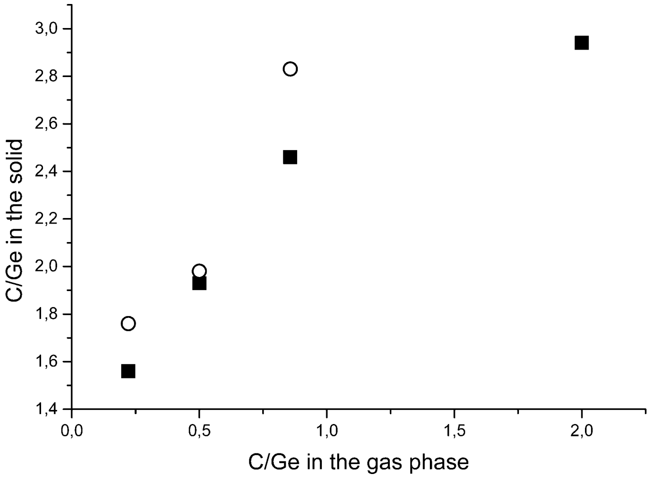

Figure 1. Variation of the C/Ge atomic ratio in the solid obtained from irradiation as a function of the C/Ge ratio in the initial gas mixture for samples of series A (open circles) and series B (solid squares).

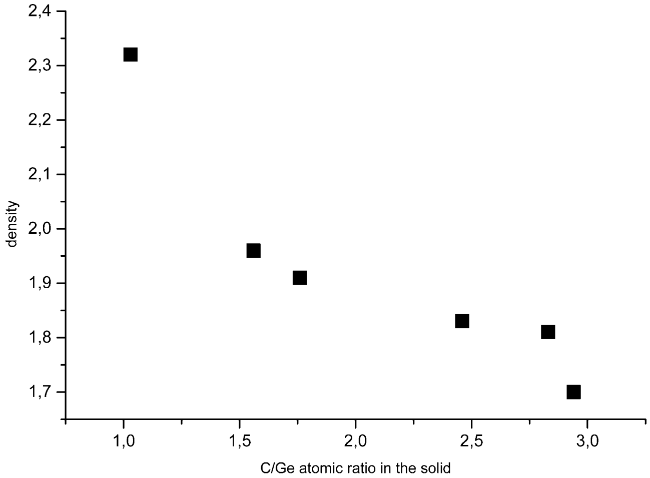

Figure 2. Density values of materials obtained from irradiation of mixtures with various C_2H_2 percentages as a function the C/Ge atomic ratio in the solid.

the carbon content and the amount of solid products increase with C_2H_2 percentage in the mixture.

Figure 1 shows the variation of the C/Ge atomic ratio in the solid obtained from irradiation as a function of the C/Ge ratio in the initial gas mixture.

In the solids obtained from systems of A series (with the vials bottom positioned out of the main X-ray trajectory) the C/Ge ratio is a little higher than in the solids obtained from analogous systems of B series (vials bottom on the X-ray trajectory); to the contrary, the total solid quantity (Table 2) is lower and this difference increases when the ethyne percentage is enhanced.

The density of various materials, measured with a Berman balance (vs toluene), does not seem to be dependent on the vial position during irradiation and is only related to the C/Ge atomic ratio in the solid (Figure 2). The values range between 2.32 and 1.70 when the ethyne percentage varies from 5 to 50% in the irradiated gaseous mixture.

The most remarkable difference among solids obtained from A series and B series experiments is their consistency. In fact, when the vial bottom on which the material is deposited is not on the X-rays trajectory, the solid obtained is a powder which can be easily removed whereas the solid obtained with the vial bottom directly under X-ray bombardmentis compact and well-adhered to the vial wall. It is particularly interesting that these last materials (B series) can be recovered from the vial wall as yellow chips about 1 cm^2 large when obtained from irradiated starting mixtures containing 30% of ethyne, while when obtained from mixtures with 50% of ethyne they are recovered as white foils as wide as the bottom vial and so elastic that they can be rolled up. The same behavior is obtained if, before irradiation, we put on the vial bottom substrates of polyethylene or other plastics: the materials (if from B series) adhere to these substrates.

These results indicate that when the vial bottom is under the direct beam rays, the grafting phenomenon takes place and the polymerization process is initiated by radicals produced in the substrate. It causes a continuos growth of the solid which originates compact layers.

The grafting is favored by the presence of ethyne; in fact, when its percentage is higher, the solid is more compact and abundant. When the vial bottom is out of the direct beam rays, the polymer is likely produced in the gaseous phase and precipitate via gravity, leading to dusty solids.

The total amount and the carbon content of solids obtained from GeH_4/C_2H_2 mixtures increase when the hydrocarbon percentage in the reaction mixture is enhanced (up to 50%) as observed for solids obtained from[17] GeH_4/C_2H_4. On the contrary, if saturated hydrocarbons are used,[21−24] the carbon content in the solids increased, but the solid yield decreases with increasing hydrocarbon content. This finding may indicate that in systems containing saturated hydrocarbon the polymerization reactions are due mainly to the GeH_x ($x = 1-3$) species. To the contrary, if ethene or ethyne are used as the reacting gas, the molecules or activated species of the hydrocarbon play a fundamental role in the polymerization process.

The compounds obtained from irradiation of mixtures with ethyne exhibit C/Ge atomic ratios and solid yields higher than the ones of the compounds obtained from mixtures with ethene at a comparable percentage. In particular, the difference among the solid amounts obtained from reacting mixture with C_2H_4 and C_2H_2 increases with the hydrocarbon percentage. In fact, 10 and 20 mg of product are obtained from mixtures with 8 and 30% of ethene, respectively, but the solid amounts obtained with similar amounts of ethyne are 4 and 10 times higher, respectively.

Moreover, ethyne exhibits a higher reactivity than ethene toward germane. In fact, for GeH_4/C_2H_4 mixtures, the percentage of germane decomposed (considering both volatile compounds and condensed phase products) varies from 0.5 to 2.0%[17] of germane initially present in the mixture when ethene ranges from 3 to 30%, while it varies from 8.1 to 22.2% with ethyne

---

(21) Antoniotti, P.; Benzi, P.; Castiglioni, M.; Operti, L.; Volpe, P. *Chem. Mater.* **1992**, *4*, 717−720.

(22) Benzi, P.; Castiglioni, M.; Volpe, P. *J. Mater. Chem.* **1994**, *4*, 1067−1070.

(23) Benzi, P.; Castiglioni, M.; Truffa, E.; Volpe, P. *J. Mater. Chem.* **1996**, *6*, 1507−1509.

(24) Antoniotti, P.; Benzi, P.; Castiglioni, M.; Operti, L.; Volpe, P. *Radiat. Phys. Chem.* **1996**, *48*, 457−462.

Table 3. Percentage of Decomposed Germane and Ethyne in Solid and Gaseous Products (Series B)

mixture (ethyne percentage)	GeH_4[b] in the solid	C_2H_2[a] in the solid	GeH_4[b] in gas	C_2H_2[a] in gas
10%	3.8%	23.5%	4.3%	20.1%
20%	10.3%	39.8%	12.5%	25.6%
30%	19.8%	54.7%	2.4%	2.9%
50%	42.7%	62.8%	3.7%	1.9%

[a] Percentage of decomposed ethyne in solid or gaseous compounds with respect to the ethyne initially in the mixture. [b] Percentage of decomposed germane in solid or gaseous compounds with respect to the germane initially in the mixture.

ranging between 10 and 30%. The percentage becomes 46.4 if ethyne is 50%.

In Table 3 the millimoles of decomposed germane and ethyne (found as solid and gaseous compounds) are reported.

These data show that if the ethyne percentage is increased, the polymerization reactions leading to solid products are favored with respect to reactions leading to gaseous compounds.

In fact, considering mixtures with 10 and 20% of ethyne, the percentages of ethyne (20.3 and 25.1%) and germane (4.3 and 12.3%) decomposing to gaseous products, with respect to their quantity initially present in the mixtures, are comparable with the percentage of ethyne (23.5 and 39.8%) and germane (3.77 and 10,3%) leading to solid products. In contrast, when mixtures with 30 or 50% of ethyne are irradiated, the percentage of reactants found as solid products are much higher with respect to that found as gaseous products.

In a previous paper[25] we have investigated the reaction mechanisms involved in systems containing germane and ethyne in different ratios under radiolysis and some hypotheses on ion reaction mechanisms and radicalic reactions have been reported.

During irradiation both ionic and radical species may be involved in the formation of volatile and condensed products. The results obtained have shown that for each ion about six radicals are formed from germane and two radicals from ethyne, thus indicating that radical reactions give the major contribution to the products formation.

For the most probable starting reactions of the polymerization we have hypothesized

$$GeH_4 + C_2H \rightarrow HC{\equiv}C{-}GeH_y + (4-y)H \quad (y = 0-2) \quad (1)$$

$$C_2H_2 + GeH_x \rightarrow HC{=}CH{-}GeH_z + (x-z)H \quad (x = 1-3,\ z = 0-2) \quad (2)$$

where the products may react further, leading to chain propagation.

In the mixture with germane in excess, the most probable following reactions should be with GeH_4, leading to a solid polymer with a carbon content lower than that determined experimentally.

Therefore, on the basis of mass spectrometric experiments (showing formation of $C_4H_m^+$, $m = 1-4$ ions prior to reactions with germane to give Ge−C containing ions), we suggested the reaction

$$C_2H + C_2H_2 \rightarrow C_4H_3 \quad (3)$$

that can be followed by recombination with a hydrogen radical to form C_4H_4.

These two species, C_4H_3 and C_4H_4, can substitute C_2H and C_2H_2 in reactions 1 and 2, respectively, giving

$$GeH_4 + C_4H_3 \rightarrow C_4H_3GeH_y + (4-y)H \quad (y = 0-2,\ 4) \quad (4)$$

$$C_4H_4 + GeH_x \rightarrow C_4H_4GeH_z + (x-z)H \quad (x = 1-3,\ z = 0-2) \quad (5)$$

and leading carbon-rich materials as found.

Morphology, Bonding, and Structure. All the samples were analyzed by EPR and X-ray diffraction: the spectra of the compounds do not show any crystallinity; that is, the material is in the amorphous state, whereas the EPR analysis evidences the absence of dangling bonds. Parts (a) and (b) of Figure 3 show the SEM pictures of solids obtained from irradiation of mixtures with 10 and 50%, respectively, of ethyne of series B.

The solids are obtained as spherical aggregates which appear isolated in the solid obtained from a mixture with 10% of ethyne, whereas they are bounded together (fused-like) in the solid obtained with 50% of ethyne. This is in agreement with the observed different consistency (powder and foil, respectively) of the solids as reported above.

It is known[26] that amorphous silicon and germanium obtained from decomposition of hydrogen-containing gaseous precursors have a very low density of dangling bonds because these are saturated with hydrogen atoms. This passivation strongly affects the optical and electrical properties of the material. Following results of EPR spectroscopy, as reported above, the materials under examination have no dangling bonds. Therefore, IR spectroscopy was used to investigate the hydrogen-bonding configurations together with the structures of the a-GeC:H materials obtained.

In Figure 4 a typical IR absorption spectrum of the solid obtained from irradiation of a mixture with 10% of ethyne and vial bottom on the main X-ray trajectory is shown. In the same figure are also reported for comparison the spectra of both the solid obtained by irradiation of a mixture with 15% of ethene (having a comparable composition) and of pure monogermane.

Figure 5 shows the IR spectra of the solids obtained from irradiation of mixtures with C_2H_2 ranging from 10 to 50% and positioning the vials bottom on the main X-ray trajectory. The spectra have been superimposed and divided into two regions depicted in Figure 5, from 3050 to 2700 cm^{-1} (a) and from 1500 to 400 cm^{-1} (b).

In the 3050−2700-cm^{-1} range (Figure 5a), absorptions of CH_n ($n = 1-3$) are expected. All the solids exhibit three partially overlapped bands. The deconvoluted signals are around 2930, 2893, and 2860 cm^{-1}. From Figure 4 it is evident that the solid obtained from irradiation of the mixture with ethene exhibits two

---

(25) Benzi, P.; Bottizzo, E.; Operti, L.; Rabezzana, R.; Vaglio, G. A.; Volpe, P. *Chem. Mater.* **2002**, *14*, 2506−2513.

(26) Brodsky, M. H.; Cardona, M.; Cuomo, J. J. *Phys. Rev. B* **1977**, *16*, 3556−3571.

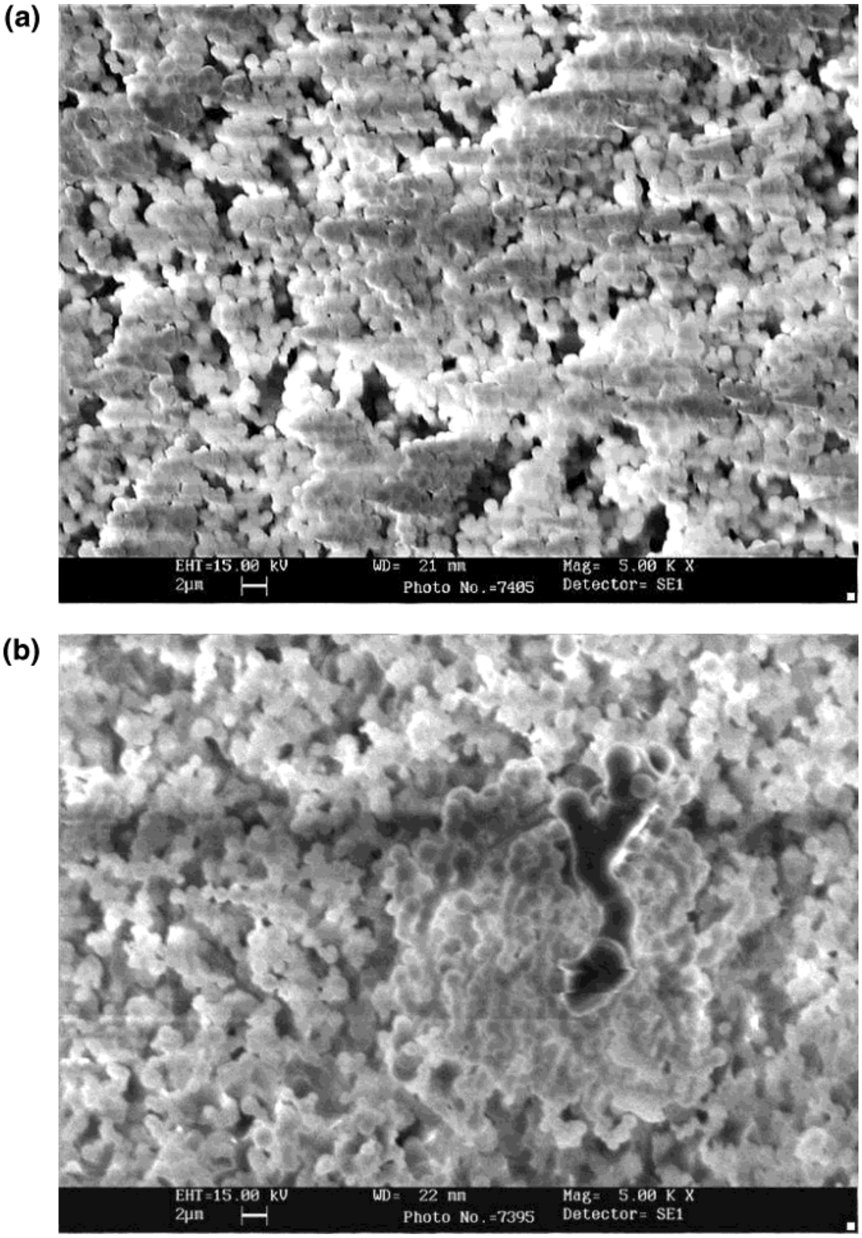

Figure 3. (a) SEM pictures of solids obtained from irradiation of mixtures with 10% of ethyne. (b) SEM pictures of solids obtained from irradiation of mixtures with 50% of ethyne.

signals around 2955 and 2872 cm^{-1}, attributable to stretching modes of the CH_3 groups,[3,12,27−33] which are not present in the spectrum of the solid obtained from ethyne, despite the very similar composition. This suggests that the materials obtained from radiolysis with ethyne only contain mono- and dihydrocarbon groups and we attribute the signals around 2930 and 2860 cm^{-1} to in and out phase vibrations of hydrogen atoms in the CH_2 group and the signal at ca. 2893 cm^{-1} to CH stretching mode.[31,33]

Moreover, the peak at 2893 cm^{-1} always exhibits the highest intensity whereas the literature data report[31,33] that the absorption intensity of the CH group is low if compared with those of CH_2 or CH_3 groups, thus indicating that the CH groups are predominant.

A signal around 2800 cm^{-1} is also present, but it is not attributed yet.

Signals in the 3050−2700-cm^{-1} range increase with the solid carbon content. As expected, however, the normalized integrated absorption I of deconvoluted signals, defined by[3,29]

$$I = \int \alpha(\omega)\omega/\mathrm{d}\omega$$

(where $\alpha(\omega)$ is the absorption coefficient at wavenumber ω), indicates that the increase of the peak at 2893 cm^{-1},

---

(27) Shinar, J.; Wu, H. S.; Shinar, R.; Shanks, H. R. *J. Appl. Phys.* **1987**, *62*, 808.

(28) Rübel, H.; Schröder, B.; Fuhs, W.; Krauskopf, J.; Rupp, T.; Bethge, K. *Phys. Status Solidi B.* **1987**, *139*, 1351.

(29) Cardona, M. *Phys. Status Solidi* **1983**, *118*, 463.

(30) Vilcarromero, J.; Marquez, F. C.; Freire, F. L., Jr. *J. Appl. Phys.* **1998**, *84*, 174−180.

(31) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975; pp 13−36.

(32) Schrader, B. *Infrared and Raman Spectroscopy*; VCH: Weinheim, 1995; pp 192−195.

(33) Dolphin, D.; Wick, A. *Tabulation of Infrared Spectral Data*; John Wiley & Sons: New York, 1977; pp 1−2.

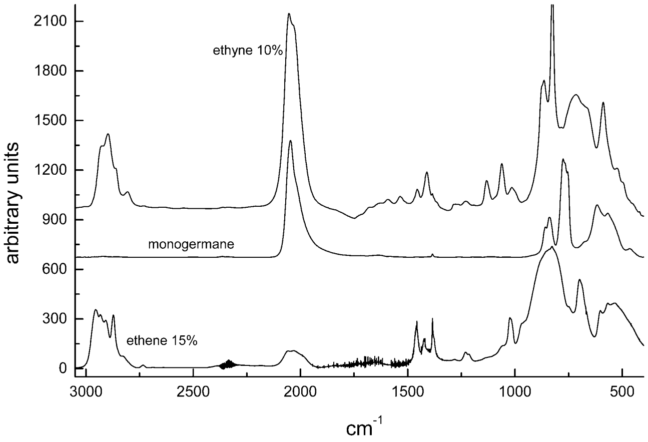

Figure 4. IR absorption spectra of the solids obtained from irradiation of mixtures with 10% (and vial bottom on the main X-ray trajectory) of ethyne, with 15% of ethene and of pure monogermane.

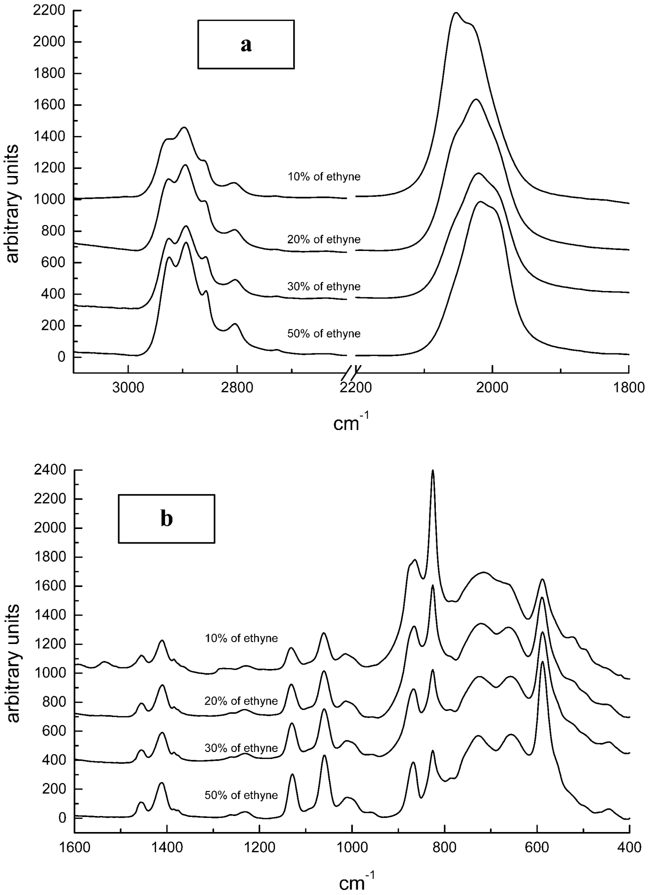

Figure 5. IR spectra of the solids obtained from irradiation of mixtures with C_2H_2 ranging from 10 to 50% and vial bottom on the main X-ray trajectory. The spectra are been superimposed and divided into two regions depicted in a and b.

attributed to stretching of CH groups, is higher than the increase of the peak at 2930 cm^{-1}, attributed to stretching of CH_2 groups. This trend is in agreement with the hypothesis reported above on the mechanism of chain propagation leading to solids products, which involves the preliminary formation of highly unsaturated C_4H_3 and C_4H_4 species.

In the range 2150−1900 cm^{-1} (Figure 5a) the signals are an envelope of partially overlapped bands: the signal deconvolution exhibits two bands around 2058 and 2025 cm^{-1} for solid obtained with 10% of ethyne and a third band around 1992 cm^{-1} is observed in the IR spectra of the solids obtained from mixtures with ethyne content ranging from 20 to 50%. These bands are attributable to Ge−H stretching mode[12,13,17,27−30,34−36] in the GeH_n ($n = 1-3$) groups, but the interpretation of the substructure is complicated by the possible shift of these bands for the changes in the electronegativity of the nearest neighbors to the vibrating group.[3,37−40] In fact, the presence of carbon atoms bound to germanium atoms strengthen the bonds stretching due to the higher electronegativity of carbon with respect to Ge. Moreover, the bands position can be affected by the presence of internal surfaces analogously to a-Ge:H.[29,34] On the basis of what is reported about analogous a-GeC:H alloys[12,13,17,28−30,34,35] and considering the estimated influence of one, two, or three neighboring carbon atoms on the stretching frequencies of GeH and GeH_2,[17] the band around 2056 cm^{-1} can be attributed to GeH_3, C_2-GeH_2, or C_3GeH; the band around 2026 cm^{-1} to GeC_2-GeH or $GeCGeH_2$ and the band around 1995 cm^{-1} can be assigned to Ge_2CGeH or Ge_2GeH_2. The unambiguous attribution of the single bands is impossible, but it is reasonable to suppose that each band is the sum of the contributions of the corresponding groups.

The integrated absorption of deconvoluted signals does not exhibit a regular trend with the increase of solids carbon content and the frequency of the single signals varies about 6−10 cm^{-1}. This is probably due to the variation of solid composition which causes a variation of the contribution of the different groups to each signal.

Figure 5b shows the spectra between 1500 and 400 cm^{-1}. In this region the presence of many bands, some of which are broad and partially overlapped, make the interpretation difficult.

In the wavenumber region between 500 and 900 cm^{-1}, the $GeCH_n$ ($n = 1, 2$) and GeH_2 bending modes,[3,27,29] besides Ge−C stretching and Ge−H wagging modes, are expected. All the spectra reported in Figure 5b exhibit two peaks around 590 and 655 cm^{-1}, whereas in the spectrum of the unalloyed a-Ge:H (Figure 4) two bands at 565 and 615 cm^{-1} are present and attributable to GeH wagging modes.[29,34] Drüsedau et al.[3] found in the same zone of a-Ge:H (only containing monohydride groups) a single band at 555 cm^{-1}, which shifts at 597 cm^{-1} for a-GeC:H samples, having analogous composition to our solids, in very good agreement with our results. Hence, we agree with Drusedau et al., attributing the shift of the 565-cm^{-1} band to 590 cm^{-1} to both the shift of GeH wagging mode for the increasing C content[3] and the appearance of a Ge−C superimposed stretching vibration.[3,41]

---

(34) Lucovsky, G. *J. Non-Cryst. Solids* **1985**, *76*, 173.

(35) Paul, W.; Jones, S. J.; Turner, W. A.; Wickboldt, P. *J. Non-Cryst. Solids* **1992**, *141*, 271.

(36) Maruyama, T.; Akagi, H. *J. Electrochem. Soc.* **1996**, *143*, 4087−4089.

(37) Egorochkin, A. M.; Sevast'yanova, E. I.; Ya. Khorshev, S.; Ratushnaya, S. Kh.; Satge, J.; Riviere, P.; Barrau, J.; Richelme, S. *J. Organomet. Chem.* **1978**, *162*, 25.

(38) Eujen, R.; Mellies, R.; Petrauskas, E. *J. Organomet. Chem.* **1986**, *299*, 27−40.

(39) Egorochkin, A. M.; Sevast'yanova, E. I.; Ya. Khorshev, S.; Ratushnaya, S. Kh.; Satge, J.; Riviere, P.; Barrau, J.; Richelme, S. *J. Organomet. Chem.* **1978**, *155*, 175.

(40) Mathis, R.; Barthelat, M.; Mathis, F. *Spectrochim. Acta* **1970**, *26*, 1993−2000.

The integrated absorption of this band increases with the solid carbon content while it should be proportional to $x(1 - x)^2$ (x being the carbon molar fraction in $Ge_{1-x}C_x$:H)[12] and have a maximum at $x = 0.33$. This suggests an increase of the solid Ge−H bond concentration.

The band at 725 cm^{-1}, which compares only in a-GeC:H alloys, is attributable to the rocking vibration of the CH_2 groups in $-CH_2-$ chains with $n > 4$.[31,32]

The absence in our samples of the band at 770 cm^{-1} observed by Drusedau et al.[3] and assigned to wagging mode of $Ge-CH_3$ units confirms the above hypothesis that our samples only contain mono- and dihydrocarbon groups.

The signals between 750 and 800 cm^{-1} can be due to both GeH_2 and to GeH_3 bending modes and to $GeCH_n$ ($n = 1, 2$) wagging mode.[3,12,27−29]

Several bands are also present in the wavenumber region between 900 and 1500 cm^{-1}.

On the basis of what is reported about analogous bands in hydrocarbons, a-GeC:H and a-SiC:H, and considering the absence of CH_3 stretching signals, the bands between 1200 and 1500 cm^{-1} can be assigned to the deformation vibrations of the groups and the bands between in the 900- and 1200-cm^{-1} range to the rocking or wagging modes of $(CH_m)_n-C/Ge$ ($m = 1, 2$; $n = 1-3$) groups.[3,17,28,31]

Optical Properties. Absorption measurements have been made at photon energies between 0.5 and 7 eV on all the solids. The optical gap values have been obtained using the common procedure of Tauc[42,43] from intercept with the x axis of the extrapolated linear part of the curve obtained by plotting $(\alpha h\nu)^{1/2}$ against the photon energy according to

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

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

The values of E_{opt} are between 0.05 and 2.41 eV and are reported in Table 2: when the solid carbon content increases, the E_{opt} value initially decreases and then increases. The variation of E_{opt} with the solid composition is related to the local bonding. If a-GeC:H is considered a sp^3-bonded binary alloy, the gap widens up with the increase of solid carbon content, which is expected due to the replacement of Ge−Ge bonds by stronger Ge−C bonds and, for $x > 0.5$ (in $Ge_{1-x}C_x$:H) by C−C even stronger bonds.[44,45] On the other hand, also C sp^2-bonding configuration must be considered for $x > 0.5$, with the introduction of weaker π-bonding states leading to a decrease of the gap.[3,9,17,45,46]

The hydrogen rule on the gap value variation must also be considered. In fact, hydrogen is found to broaden the band gap both for sp^3- and sp^2-bonded alloys.[45,46] Moreover, hydrogen promotes the formation of sp^3-hybridized C atoms over sp^2 ones, terminating any dangling bonds and thus reducing the size of graphitical cluster, increasing the gap.

Therefore, we think that the decrease of the gap value with the increase of carbon content until $x = 0.66$ is related to gap narrowing in carbon-rich compounds for the presence of C sp^2-bonded, while the gap increase observed for $x > 0.66$ is attributable to high hydrogen content.

The trend of the E_{opt} (Table 2) observed is consistent with that reported for the solids obtained from irradiation of GeH_4/C_2H_4 mixtures,[17] even if the values are considerably smaller (with respect to those of the compounds obtained with ethene and having analogous composition).

This is in agreement with the above-reported hypothesis for the reaction mechanism leading to the solid formation, which favors the formation of zones in which several C atoms are bounded together, forming a 3-fold coordinate graphite-type local environment.[9,45,46]

Conclusion

All the results indicate that the materials obtained from X-ray radiolysis of GeH_4/C_2H_2 mixtures are amorphous nonstoichiometric germanium carbide compounds.

The composition varies over a wide range by varying the ethyne percentage. Both carbon and hydrogen content increases with ethyne percentage in the irradiated mixture.

In the IR spectra, vibrational modes of CH_2 and CH groups are evident, whereas bands attributable to CH_3 groups are absent. Vibrational modes of the Ge−H, $GeCH_n$ ($n = 1, 2$), and Ge−C groups are also present. Optical gap values between 0.05 and 2.41 eV have been found. The E_{opt}, in the expected range of optical gaps, decreases with increasing carbon molar fraction, x, in the solid until $x = 0.66$ and then increases. This trend is attributable to the band gap narrowing effect of the C sp^2-bonding configuration and to the widening effect of hydrogen.

Therefore, there is experimental evidence that the use of a highly unsaturated hydrocarbon such as ethyne leads to important advantages with respect to previously examined systems. In particular, the solids obtained are stable to air; their yields are sharply higher; they are deposited as films starting from mixtures containing more than 20% of ethyne.

CM034547Z

---

(41) Breford, J. L.; Corriu, R. J. P.; Guerin, C.; Henner, B. J. L. *J. Organomet. Chem.* **1994**, *464*, 133−142.

(42) Ley, L. *The Physic of Hydrogenated Amorphous Silicon II*; Springer-Verlag: New York, 1984.

(43) Tauc, J.; Grigorovici, R.; Vancu, A. *Amorphous and Liquid Semiconductors*; Plenum: New York, 1974.

(44) *CRC Handbook of Chemistry and Physics*, 78th ed.; CRC Press: Boca Raton and New York, 1997−1998.

(45) Robertson, J. *Philos. Mag.* **1992**, *66*, 615−638.

(46) Yuan, H.; Williams, R. *Chem. Mater.* **1993**, *5*, 479−485.