# THERMOLYSIS AND MASS SPECTRA OF POLYMERIC GERMANIUM HYDRIDE PRODUCED BY γ-RADIOLYSIS

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**Abstract**—TGA, MS and DSC of a solid polymeric Ge hydride, obtained by  $\gamma$ -radiolysis of GeH<sub>4</sub>, are reported. Upon heating, it undergoes two successive weight losses at 463 and 1173 K. At 948 K two crystal phases are formed, one of them is pure germanium. Some comparisons with a-Ge: H produced via RF sputtering or glow discharge are reported.

The preparation and the elemental analysis of the solid polymeric hydride obtained by gas phase radiolysis of  $GeH_4$  have been reported already.<sup>1</sup>

This paper will give more insight on the properties and thermal behaviour of the hydride in view of its possible use for the preparation of a-Ge:H.

#### **EXPERIMENTAL**

GeH<sub>4</sub> was produced and purified as previously reported.<sup>1</sup> The purity of the compound was, from time to time, checked by mass spectrometry. The samples, at a pressure ranging from 80 to 90 KPa, were sealed in cylindrical Pyrex vials 21.0 cm high and 3.5 cm i.d., and were then irradiated in a Gammacell (Atomic Energy of Canada Ltd) for a total dose of  $8.0 \times 10^5$  Gy ( $T \sim 315$  K), as previously described.<sup>1</sup> After irradiation, the ampoules were evacuated and the dark brown solid product was recovered from the bottom of the ampoule. The product was carefully outgassed for at least 8 h, before any further treatment, to free it from any short chain volatile hydrides.

The IR spectra were collected from KBr discs using a Perkin-Elmer 580B IR spectrophotometer. Mass spectra were recorded on a Kratos MS 80 using both electron impact and chemical ionization. Thermogravimetric analysis (TGA) was performed with a Du Pont 1090 instrument and differential scanning calorimetry (DSC) using a 910 cell. X-ray analysis was performed with a wide angle Philips diffractometer using Co- $K_{\alpha}$  radiation.

For purpose of comparison, some samples of solid polymeric hydrides were obtained by wet methods using both acetic and sulphuric acid.<sup>2,3</sup>

### **RESULTS AND DISCUSSION**

A typical radiolysis run yields about 10 mg of a dark brown waxy powder: the solid germanium hydride. According to the previously reported data<sup>1</sup> the composition of the solid is  $GeH_{1.15}$ . The hydride is not soluble in ordinary solvents, is stable and does not show an appreciable change in properties

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after three months of exposure to the atmosphere. Due to the apparent stability of the compound, and the invariability of the IR and mass spectra, after months of exposure to the laboratory atmosphere, it was decided not to investigate the possibility of the formation of a transparent thin film of oxide on the surface of the material.

Samples of polygermane obtained by wet chemistry<sup>2,3</sup> and by radiolysis of  $GeH_4+O_2$  mixtures show wide IR absorption bands in the regions 3300– 2800, 1380–1030 and 800–500 cm<sup>-1</sup>, which have been attributed to OH and Ge—O (Ge—O—Ge) groups.<sup>4,5,6</sup>

The IR spectra of oxygen free radiolytic germanium hydride show absorptions at 2065, 2045, 810 and 780 cm<sup>-1</sup>, which have been attributed to Ge—H bonds.<sup>2,6,7,8</sup> As the sample is annealed under an inert atmosphere (argon) at 463 K, the intensities of the Ge—H bond absorptions decrease.

The mass spectra of the hydride are complicated due to the presence of five germanium isotopes and to its low degree of hydrogenation. Nevertheless, the mass spectrum shows, for the unannealed material, a mass distribution corresponding to units ranging from one to eleven Ge atoms, as the temperature of the ion source is raised from that of the room up to 580 K.

Figure 1 shows the average hydrogen content, per Ge atom, of the fragments observed in the mass spectrometer. When the sample is annealed at 773 K for 1 h (under argon), the fragment of the lowest m/e value observed in the mass spectrum corresponds to a cluster of seven germanium atoms with an average Ge/H ratio of 1/0.17.

TGA of the solid hydride indicates that in the 323–1173 K range, the sample undergoes a total loss of weight corresponding to 23.4% (Fig. 2). There is a 6% weight loss during an exothermic transformation (see below) at 463 K; a second mass loss occurs at 1148 K, somewhat before the melting point of germanium (1210.4 K).

The change in both the IR and the mass spectra after annealing above 463 K indicates that some Ge-H bonds have been destroyed and that hydrogen is lost by the hydride. The loss of 6% in weight upon annealing is too high to be accounted for by only hydrogen loss; in fact not even GeH<sub>4</sub> could lose 6% of its weight as hydrogen only. To identify the material released by the sample at 463 K, it has been collected and analysed by GC-MS: it consists of a mixture of  $GeH_4$ ,  $Ge_2H_6$ , and  $Ge_3H_8$ , in the 1:1.4:1.7 ratio, plus trace amounts of both isomeric tetragermanes. The average composition of the released material, calculated from the mass abundance of the fragments and the ionization potentials<sup>9,10</sup> is GeH<sub>3</sub>, as the composition could be roughly calculated from a 6% mass loss from a substance having the  $GeH_{1,15}$  composition. After annealing at 463 K the compound has the same aspect as the original hydride and undergoes a further weight loss of 17.8% (as referred to the weight after the annealing at 463 K) at 1148 K. The material released at the above temperature has been analysed by mass spectrometery and has been shown to consist of only GeH<sub>4</sub>.

DSC analysis (Fig. 2) shows a first exothermal effect around 463 K, corresponding to the loss of 6% in weight as evidenced by TGA. A second very



Fig. 1. Average hydrogen content of the fragments observed in the mass spectrum : ● unannealed samples ; ▲ samples annealed at 773 K.



Fig. 2. TGA of the polymeric hydride : —— weight loss (%); ---- weight loss derivative (%/min). DSC of the polymeric hydride : ---- heat flow.

sharp exothermal transition occurs at 948 K, which is not associated with any mass change. X-ray analysis has shown the solid to be amorphous both before and after the thermal effect at 463 K. However, the sample appears polyphasic after the transition at 948 K. The presence of two crystalline phases is evidenced in its X-ray spectrum: (a) pure germanium, diamond type structure<sup>11</sup> and (b) a second phase, giving a number of reflections. which has not yet been identified. Therefore, we conclude that the sharp exotherm at 948 K is due to crystallization of the amorphous sample involving a phase change. Two small thermal effects are also manifested in the DSC trace, as shown in Fig. 2, occurring at temperatures immediately lower than the main crystallization peak. No detailed structural analysis of their origin has been performed, but it is not unreasonable to assume that they correspond to an early crystallization of a small fraction of the sample.

The second phase present in the sample disappears after the thermal treatment at 1148 K involving the loss of  $GeH_4$ , as shown by the X-ray spectrum where only reflections due to pure Ge are present.

The absence of any IR absorption at about  $1880 \text{ cm}^{-16}$  and the presence of bands at 2065 and 2045 cm<sup>-1</sup> indicates that the compound is a kind of unsaturated, crosslinked polygermane, rather than an amorphous hydrogenated germanium.

The properties of the polygermane obtained by  $\gamma$ -radiolysis appear similar to that of the material prepared by glow discharge,<sup>12</sup> but are quite different from the properties of the compound prepared by RF sputtering.<sup>6</sup>

The bonded hydrogen atom concentration in the radiolytic polygermane, prepared at about 315 K and 80-90 KPa, is 53.5 atom %, whilst in the compound obtained by glow discharge, at the same temperature, but at a pressure three orders of magnitude lower,6 is 35 atom %. As already reported,1 also with y-radiolysis, as the pressure of the reactant gas is lowered, the percentage of the hydrogen atoms in the solid decreases. Moreover, with the glow discharge method, the hydrogen concentration seems to be correlated to the temperature of the substrate during the deposition; when the temperature is kept under 498 K the hydrogen concentration is in the 35-25 atom % range, but when it is raised to about 498 K the hydrogen concentration rapidly drops to 10-12 atom %.6 A similar trend is observed on annealing the radiolysis product: at 463 K a rapid loss of H (as germanium hydrides) is observed. The 35 K temperature difference for the two phenomena does not seem to be of relevance. taking into account the rather different preparation conditions. It should be pointed out that A.A.<sup>6b</sup> observed, in plasma deposited materials, a sharp change in the hydrogen status of the a-Ge: H vs the substrate temperature at about 473 K (which is in the 463-498 K temperature range).

Connel and Pawlich,<sup>12</sup> from the IR analysis of the material prepared at room temperature by RF sputtering, inferred that the material annealed up to 523 K does not lose hydrogen by breakage of Ge—H bonds, but rather undergoes a network reorganization. Probably, such material is more cross-linked than the radiolytic (and glow discharge) one, which indeed loses hydrogen (through Ge-hydrides) in the 463-498 K range, probably by rupture of the more hydrogenated boundary chains of the network.

Finally, in the radiolytic material a further exothermic transformation occurs at 948 K which is very rapid (see the very narrow DSC signal) and is not likely to correspond to the proposed network reorganization at 523 K occurring on the RF sputtered material.<sup>12</sup>

The last hydrogen loss (at 1148 K) by the elimination of GeH<sub>4</sub>, appears to be associated with a process, the rate of which increases with the temperature but falls abruptly as the supply of the reactant falls; this behaviour is observed in reactions where diffusion and/or evaporation are implicated. GeH<sub>4</sub> is released instead of molecular or atomic hydrogen, because the bond dissociation energy for Ge-H<sup>13</sup> is higher than for Ge-Ge.<sup>13,14</sup>

The similarity of the compounds prepared by glow discharge and  $\gamma$ -radiolysis is not surprising because in both methods highly excited states of atoms, molecules, radicals and ions could be involved even though the temperature of the gas is quite low<sup>15</sup> and of course is lower in  $\gamma$ -radiolysis than in glow discharge.

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#### REFERENCES

- R. Belluati, M. Castiglioni, P. Volpe and M. C. Gennaro, *Polyhedron* 1987, 6, 441.
- W. L. Jolly and J. E. Drake, *Inorg. Synth.* 1963, 7, 36.
- 3. W. L. Jolly and J. E. Drake, *Inorg. Synth.* 1963, 7, 37.
- T. D. Goldfarb and S. Sujishi, J. Am. Chem. Soc. 1964, 86, 1679.
- 5. S. Cradock, J. Chem. Soc. (A) 1968, 1426.
- (a) G. Lucovsky, S. S. Chao, J. Yaug, J. E. Tyler, R. C. Ross and W. Czubatyj, *Phys. Rev. B* 1985, 31, 2190; (b) J. S. Rayson and R. C. Ross, *J. Non-Cryst. Solids* 1985, 77-78, 579.
- D. A. Dows and R. M. Hexter, J. Chem. Phys. 1956, 24, 1029.
- J. E. Drake and W. L. Jolly, J. Chem. Soc. 1962, 2807.
- F. E. Saalfeld and H. J. Svec, *Inorg. Chem.* 1963, 2, 46.
- F. E. Saalfeld and H. J. Svec, *Inorg. Chem.* 1963, 2, 50.
- 11. X-ray Powder Data File. A.S.T.M., Philadelphia (1962).
- 12. G. A. N. Connell and J. R. Pawlik, *Phys. Rev. B* 1985, 31, 2190.
- M. J. Almond, A. M. Doncaster, P. N. Noble and R. Walsh, J. Am. Chem. Soc. 1982, 104, 5717.
- 14. R. A. Jackson, J. Organomet. Chem. 1979, 166, 17.
- 15. F. Cramarossa and P. Capezzuto, Material Chem. Phys. 1983, 9, 213.