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Excimer laser photolysis of tetramethylgermane

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Abstract

The ArF laser-induced photolysis of tetramethylgermane (TMG) in the gas-phase yields trimethylgermane, ethane, methane, and ethene, layers of germanium being deposited concomitantly. Trapping experiments with germane-d_4 suggest that major primary steps of the photolysis are molecular extrusions of methane and ethane from TMG.

Introduction

Studies on chemical vapour deposition (CVD) of germanium initiated by plasma, heat, or laser radiation, indicate that properties of the deposit will mostly depend on the temperature(s) of the process and on the mode of the decomposition of the germanium precursor.

Laser-induced CVD of germanium from germane or ethylgermanes has previously been carried out using either UV-laser (photolysis) or IR-laser (thermolysis) techniques [1-9]. Compounds Et_nGeG_{4-n} ($n = 1$-3) undergo photolysis by a mechanism rather different from that involved in their thermolysis: the former occurs mostly via a molecular extrusion of ethane, while the latter is dominated [8] by the radical cleavage of the Ge-C bond.

It thus appears that the chemistry of the CVD processes can be deliberately changed, not only by the selection of the organogermanium precursor, but also by the choice of the initiation mode of their decomposition. Thermal decomposition of various organogermanium compounds has been intensively studied and the information on chemical mechanisms of thermal CVD are thus available. Studies of UV photolytic behaviour of organogermanium compounds with one Ge atom in the molecule have, however, been very scarce, and except for those described in refs. 9 and 10, they relate only to the liquid phase [11,12].

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Thermal decomposition of tetramethylgermane (TMG) has been much studied in wall-less [13], static [14], and flow [14,15] reactors, and in a shock-tube [16]. On the other hand, the photoinitiated decomposition of TMG for the deposition of germanium was only very briefly reported [17] about 30 years ago, and no laser-induced decomposition study of TMG has yet been published.

In this paper we report on UV-laser-induced CVD of germanium from TMG, we clarify the photolytic decomposition mode of TMG, and describe the properties of deposited germanium layers.

Experimental

Gaseous samples of TMG were photolysed by use of a Questek series 2000 excimer laser operating at 193 nm with a repetition frequency of 20 Hz. Experiments were carried out in a glass reactor, which consisted of two orthogonally positioned tubes (2 cm in diameter); fused quartz plates were mounted at the ends of the shorter (6 cm) tube and NaCl windows were affixed to the ends of the longer one (15 cm). The reactor had a valve for connection to a standard vacuum line and a side-arm with a rubber septum. The unfocussed beam (energy fluence 160 mJ, FWHM *ca.* 15 ns) was spatially filtered through a slit (1 cm diameter) and entered the reactor through the quartz window.

The progress of the photolysis was monitored directly in the reactor by use of an FTIR (Perkin–Elmer, model 1710) spectrometer. The pressure of TMG was determined using the absorption band at 1245 cm^{-1} (absorption coefficient 0.031 kPa^{-1} cm^{-1}), which does not interfere with the bands of photolysis products. Methane, ethene, and trimethylgermanes were monitored at 1306 cm^{-1} (0.0047 kPa^{-1} cm^{-1}), 950 cm^{-1} (0.014 kPa^{-1} cm^{-1}) and 2041 cm^{-1} (0.11 kPa^{-1} cm^{-1}), respectively. Final amounts of methane, ethene, and ethane were determined by gas-chromatography (Packard model 427 chromatograph with FID and alumina column).

Laser photolysis of a TMG–germane-d_4 mixture was carried out under the conditions used for laser photolysis of TMG. Photolysis of the acetone–germane-d_4 mixture using a water-cooled, medium-pressure, silica-jacketed Hanovia UV lamp was conducted in the reactor for the laser-induced experiments. The changes in concentrations in these mixtures were also monitored by FTIR spectroscopy using absorption bands at 1217 cm^{-1} (acetone), 1564 cm^{-1} (germane-d_4), 1157 and 2199 cm^{-1} (methane-d_1, see ref. 18), and also by gas-chromatography. Absorption coefficients of pure, authentic samples at these wavenumbers were, in the order given above, 0.033, 0.059, 0.0013, and 0.0020.

TMG was prepared by Grignard synthesis from tetrachlorogermane and methylmagnesium iodide [19,20] and distilled from the reaction mixture. Repeated distillation gave a product which was pure as judged from its ^1H NMR and IR spectra. Germane-d_4, obtained by the reaction of germanium tetrachloride with lithium aluminium deuteride [21], contained less than 5% germane. Trimethylgermane was prepared by treatment of trimethylbromogermane with lithium aluminium hydride [19]. Ethane, ethene, methane, and acetone were purchased from Aldrich and methane-d_1 was made by deuterolysis of methylmagnesium iodide [18]. The UV spectra of gaseous TMG, germane-d_4, and trimethylgermane contained in the reactor were recorded by use of a Philips PU 8720 UV–VIS scanning spectrophotometer.

The deposited film was analysed by FTIR spectroscopy and also by Rutherford back-scattering analysis on a KN 3000 van der Graaf accelerator (H.V. Engineering, Inc.).

Results and discussion

TMG can be photolysed by an ArF laser since its absorptivity at the irradiating wavelength (193.3 nm) is 0.10 kPa^{-1} cm^{-1}. Upon initiation of the laser radiation, TMG (1.2 or 2.3 kPa) is decomposed into gaseous methane, ethane, trimethylgermane and ethene. These compounds are major products, and are accompanied by traces only of C_3 and C_4 hydrocarbons. A grey material is deposited simultaneously over all of the inside of the reactor. Dark layers covering the entrance plate are detrimental to the progress of the photolysis, since they are opaque to laser radiation and cause a gradual decay of laser power within the reactor. Relative amounts of the gaseous products do not change much with the extent of conversion. The methane-to-photolysed TMG ratio at about 10% photolysis is 1.1 or 0.95 depending on the initial TMG pressure (1.2 and 2.3 kPa, respectively). This ratio slowly decreases in the course of the reaction (Fig. 1). The yield of ethene is constant during the photolysis. Trimethylgermane, identified by its characteristic infrared absorption [22], is a minor product, the proportion of which increases very slowly as the photolysis progresses. The final amounts of ethane (Table 1) exceed by about 1.5 times those of methane.

These products can be formed via several photolytic pathways (Scheme 1). It is conceivable that methane and ethane are formed via the H-abstraction and

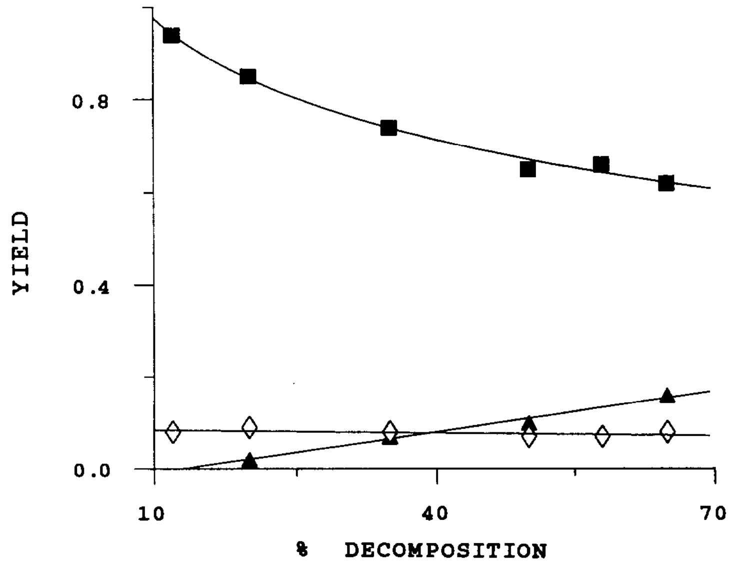


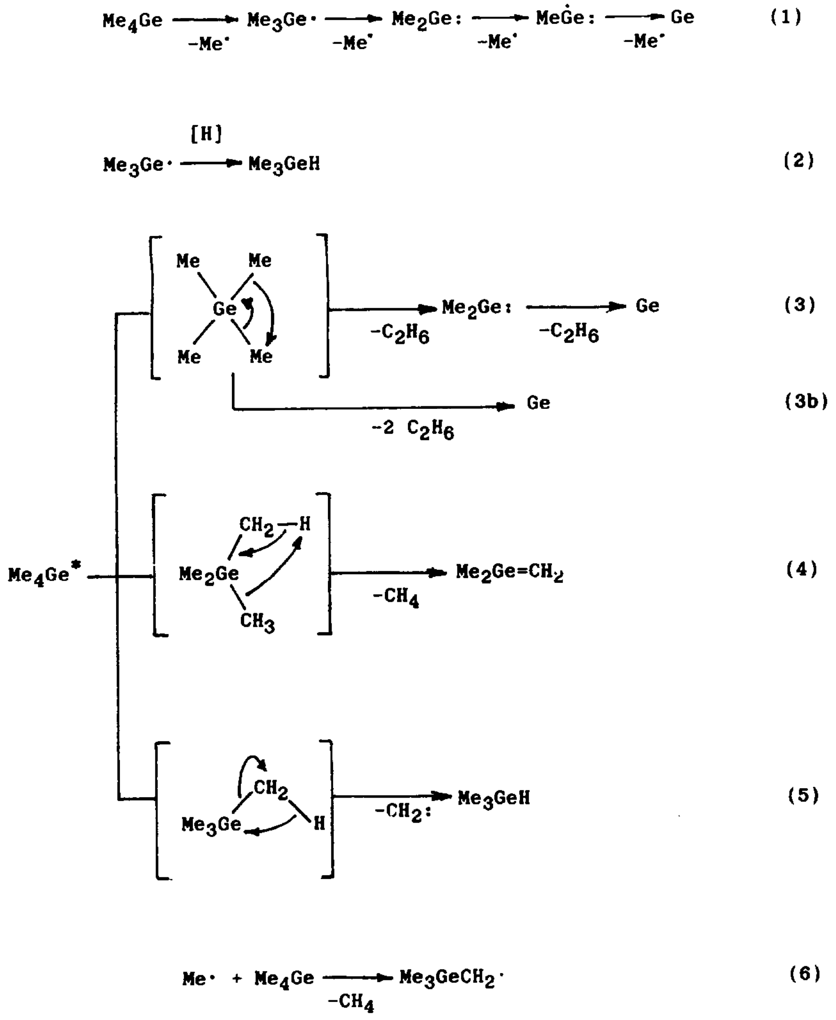
Fig. 1. Product yield as a function of percent decomposition of TMG (2.3 kPa) (■, CH_4; ◇, C_2H_4; ▲, Me_3GeH. Yield = moles of product/moles of decomposed TMG).

Table 1

Product distribution in laser photolysis of TMG and Hg-lamp photolysis of acetone

Irradiated system (kPa)	Conversion (%)	Reaction products (kPa)
TMG (2.3)	68	CH_4 (1.2), C_2H_4 (0.1), Me_3GeH (0.2), C_2H_6 (1.8)
TMG (2.2) GeD_4 (3.9) [a]	50	CH_4 (1.3), CH_3D (0.2), Me_3GeH (0.1), C_2H_6 (0.8)
MeCOMe (2.6) GeD_4 (3.8) [b]	45	CH_4 (*ca.* 0.1), CH_3D (1.7), C_2H_6 (*ca.* 0.1), CO

[a] GeD_4 depleted to 3.6 kPa, [b] GeD_4 depleted to 3.3 kPa.



Scheme 1.

recombination reactions of methyl radicals, which are produced by successive cleavage of the Ge–C bonds (eq. 1). This pathway would be analogous to that in the thermolysis of TMG [13,16], and it would be consistent with the slow decrease in the CH_4 yield as the photolysis progresses, since the abilities of $CH_3^{\cdot}$ radicals to abstract hydrogen from TMG [23] and hydrocarbons [24,25] are very alike. Trimethylgermane could thus possibly be assumed to arise from the abstraction of hydrogen by the $Me_3Ge^{\cdot}$ radical from TMG and/or the hydrocarbons that are formed in the course of the photolysis (eq. 2). The steady increase in the amount of Me_3GeH seems to be in accord with this assumption. However the following observations show that this interpretation is incorrect.

Germyl radicals possess only a very small ability to abstract hydrogen from alkanes [26–28], whereas organic radicals are known to abstract hydrogen from the Ge–H bond of triorganyl hydrides very much faster than from C–H bonds. (The only reaction between alkyl radicals and R_3GeH compounds is the abstraction of the hydrogen from the Ge–H bond [25,29–31].) These facts imply that $CH_3^{\cdot}$ radicals, if liberated during the TMG photolysis, would preferentially react with Me_3GeH and so remove it from the reaction mixture, which is not the case *. The role of radical reactions in the production of methane and ethane cannot therefore be dominant.

The only alternative pathway for the formation of these hydrocarbons involves a molecular expulsion of ethane from TMG (and/or perhaps also from dimethylgermylene, eq. 3) and a molecular expulsion of methane from TMG (eq. 4). This mechanism is rather unusual, but can be facilitated by the presence of an excess of energy in the TMG after absorption of laser photon(s). The energy delivered by a single photon at 193 nm corresponds to *ca.* 620 kJ/mol and is much in excess of that needed for the cleavage of the Ge–C (*ca.* 240 kJ/mol) [32] or the C–H (*ca.* 410 kJ/mol) bond. The irradiation parameters are compatible with the laser intensity of *ca.* 2 MW cm^{-2}, which suffices to induce two-photon processes. These can lead to population of high-energy excited states of TMG which can facilitate simultaneous cleavage of two (or more) bonds. We can thus assume that the fragments generated will recombine before they escape from the molecular sphere. The following observations on laser-induced photolysis of TMG and Hg-lamp-initiated photolysis of acetone, both examined in the presence of germane-d_4 (Table 1), are consistent with this view.

Germane-d_4 shows lower absorptivity at 193.3 nm (0.02 kPa^{-1} cm^{-1}) than TMG. Its photolysis in a mixture with TMG should therefore be slower than that of TMG, and germane-d_4 should act mostly as an efficient scavenger of methyl radicals to yield methane-d_1. The radical and molecular mechanisms of the formation of CH_4 and C_2H_6 should thus be distinguishable by these scavenging experiments and the occurrence of methyl radicals during the photolysis would be detected by the characteristic infrared absorption of CH_3D at 1157 and 2199 cm^{-1}. First we examined the scavenging ability of GeD_4 during the Hg-lamp-photolysis of acetone, which is known [24] to be an efficient source of $CH_3^{\cdot}$ radicals. A

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* We note that Me_3GeH (2.2 kPa) does not show detectable absorption at 193 nm, and that it was photolysed (23% conversion) into germanium, C_2H_6 (0.5 kPa), CH_4 (0.4 kPa) and C_2H_4 (*ca.* 0.1 kPa) about 5 times slower than TMG.

high yield of methane-d_1 and a very low yield of methane and ethane show that $CH_3^{\cdot}$ radicals were almost completely trapped by germane-d_4 (see Table 1). Conversely, laser photolysis of the TMG–GeD_4 mixture affords mostly methane and ethane and gives CH_3D in only very small amounts (Table 1). Our results (Table 1) confirm the prediction that the role of radical processes in the laser photolysis of TMG is rather small, and imply that the extrusion of CH_4 and C_2H_6 from TMG takes place by a molecular mechanism (eqs. 3 and 4). It is noteworthy that a similar intramolecular mode of ethane formation was recently suggested for the laser photolysis of trimethylalane [33] and trimethylarsine [34], and also suggested for the surface-assisted thermolysis of TMG and some other Group IVA metal methyls [13].

In view of this support for the molecular extrusion reactions from a highly excited TMG, we also suggest that trimethylgermane is not formed by the unlikely reaction (eq. 2), but by a three-centre elimination of carbene (eq. 5). Ethene, formed in a low yield, cannot be generated by the photolysis of ethane [9], but it can arise from the dimerisation of carbene.

We note that mercury-photosensitised decomposition of TMG [10], occurring via the cleavage of the C–H bonds and leading to the formation of molecular hydrogen and 1,2-bis(trimethylgermyl)ethane, should be initiated from the first triplet state. Methane produced [10] in this photolysis at a higher intensity of the irradiation can perhaps be formed from the first singlet state. We cannot specify the effective electronic state of TMG reached in our experiments, but can think it likely that TMG will undergo molecular decompositions from the second singlet or triplet. Photophysical studies are needed to verify this supposition, but several laser-initiated reactions from higher electronically excited states have already been observed [35–37] in the liquid-phase for complex organic molecules.

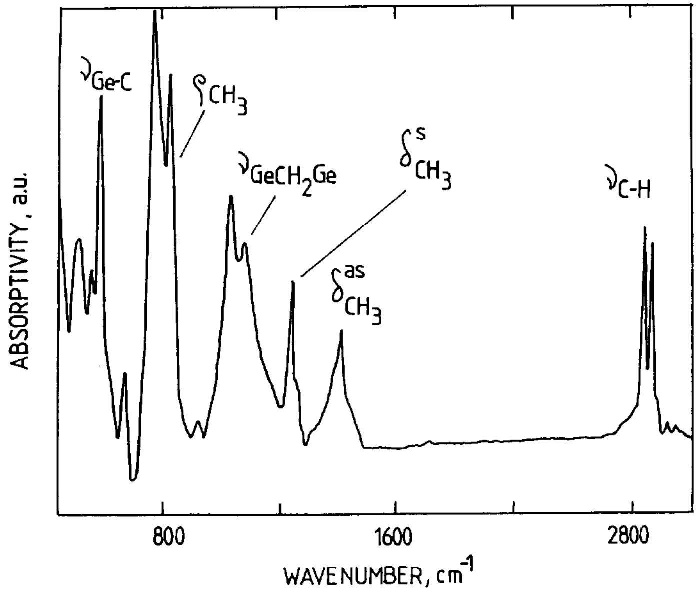

Fig. 2. FTIR spectrum of the material deposited on the reactor surface.

The extent of secondary reactions, such as those of $Me_2Ge^{\cdot\cdot}$ [16], $Me_2Ge=CH_2$, or $Me_3GeCH_2^{\cdot}$ [13], leading to the formation of organogermanium polymers, may be judged from the yields of gaseous products (Table 1) and from the FTIR spectrum of the material deposited on a KBr plate present in the reactor during the irradiation of TMG. The gaseous products correspond to about 80–90% of the decomposed TMG. The FTIR spectrum of very tiny non-volatile droplets (591, 778 823, 1033, 1234, 1411, 2904, and 2988 cm^{-1}) can be interpreted as indicated in Fig. 2, and the absorption band at 1033 cm^{-1} assigned to the $\nu(GeCH_2Ge)$ vibration [38,39]. It therefore appears that although polymerisation reactions of the above species play only a very minor role they cannot be disregarded. Back-scattering analysis of the deposit formed on the window of the entrance reactor reveals only the presence of germanium (density 0.397×10^{18} atoms cm^{-2}). We infer from this that the laser photolysis of TMG results in almost complete stripping of organic substituents from germanium and, leads to minor formation of organogermanium polymers, which can remain unchanged only when deposited in areas outside the laser beam.

The technique is useful for the deposition of uncontaminated germanium films on quartz surfaces.

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