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IR laser-induced synthesis of nanostructured gemanium telluride in the gas phase

Josef Pola[1]*, Dana Pokorná[1], María Jesús Diánez[2], María Jesús Sayagués[2], Zdeněk Bastl[3] and Vladimír Vorlíček[4]

[1] Laboratory of Laser Chemistry, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 16502 Prague, Czech Republic
[2] Instituto de Ciencias de Materiales de Sevilla, Centro mixto CSIC-US, Avda. Américo Vespucio s/n, 41092 Seville, Spain
[3] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 18223 Prague 8, Czech Republic
[4] Institute of Physics, Academy of Sciences of the Czech Republic, 18040 Prague 8, Czech Republic

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The gas-phase synthesis and chemical vapour deposition of nanostructured germanium telluride has been achieved for the first time. The pulsed IR laser irradiation of gaseous $(CH_3)_4Ge–(CH_3)_2Te–SF_6$ mixtures results in homogeneous decomposition of both organometallics and formation of $GeTe_x$ ($x = 1, 2$). The amorphous $GeTe_2$ and crystalline GeTe were identified by Raman and X-ray photoelectron spectroscopy and by electron diffraction. Their formation is explained by an intermediacy of germanium and tellurium clusters and by reaction between these clusters in a hot laser-induced zone. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: laser-induced decomposition; dimethyl tellurium; tetramethylgermane; chemical vapour deposition; nanostructured germanium telluride

INTRODUCTION

There is continuing interest in synthesis of nano-sized metal chalcogenides (e.g. see Ref. 1), whose properties depend on their shape and size and are promising for many applications. Metal tellurides are appealing for use as thermoelectric and optical data storage devices. The bulk compounds were prepared directly from the elements through solid-state reaction at high temperatures,[2] by repeated cold-pressing,[3] or thermolysis of specially synthesized organometallics containing both metal and chalcogene atoms,[4–6] whereas their nanoparticles were obtained by reactions between the elements in liquid ammonia,[7] through solvothermal routes[8–13] (assisted by ultrasound[9] or microwaves[12]) and by pyrolysis of organometallic reagents through injection into a hot coordinating solvent.[14]

Large crystals of germanium telluride (GeTe) were prepared by the Czochralski technique through heating the lumps of germanium and tellurium to several hundred degrees Celsius,[15,16] by the vapour–liquid–solid growth method,[17] or by vapour-phase epitaxy through high-temperature reaction between dimethylditellurium and dimethylcadmium.[18] Amorphous and crystalline GeTe films, usable in optical storage applications, can be prepared by evaporation of or sputtering in amorphous, crystalline or epitaxial form (e.g. Refs 19–21).

Surprisingly, no synthesis of crystalline or amorphous nanoparticles of GeTe by procedures used for other nanoscopic metal chalcogenide particles has yet been reported, and the nanocrystallline structures produced in amorphous GeTe films by electron radiation[22] remain the only system related to this topic.

Here, we report on the gas-phase synthesis and chemical vapour deposition of nanostructured GeTe, which was achieved by IR laser irradiation of gaseous mixtures of $(CH_3)_4Ge$, $(CH_3)_2Te$ and sulfur hexafluoride (SF_6).

The technique of IR laser radiation for inducing homogeneous gas-phase thermal decompositions[23–25] is known as 'laser-powered homogeneous pyrolysis' (LPHP). It has been applied in studies of many decompositions of organic and organometallic compounds[26] and in studies of chemical vapour depositions of various elements[25,27] and organometallic polymers.[28] We show that this technique can find an

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*Correspondence to: Josef Pola, Laboratory of Laser Chemistry, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 16502 Prague 6, Czech Republic.
E-mail: pola@icpf.cas.cz
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important application in the gas-phase synthesis of nanosized inorganic compounds when clusters of two different elements, simultaneously generated in the gas phase from the LPHP of two different precursors, react with each other.

We report on the pulsed CO_2 laser heating of an inert SF_6 absorber in a gaseous mixture with two non-absorbing organometallics ($(CH_3)_4Ge$ and $(CH_3)_2Te$), which leads to the gas-phase generation of germanium and tellurium clusters and the gas-phase formation and deposition of nanostructured GeTe and $GeTe_2$.

EXPERIMENTAL

The laser irradiation experiments were carried out using a transversely excited atmospheric (TEA) CO_2 laser (Plovdiv University) operating at the P(20) line of the $00^01 \rightarrow 10^00$ transition (944.19 cm^{-1}) with a repetition frequency of 1 Hz and pulse energy of 0.8 J incident on 2 cm^2. The gaseous samples of $(CH_3)_4Te$–(CH_3) $_4Ge$–SF_6 (1 : 6 : 8 ratio and total pressure 10 kPa) were irradiated in a reactor (volume 140 ml) that was equipped with a sleeve with rubber septum and PTFE valve and consisted of two orthogonal positioned Pyrex tubes (both 3 cm in diameter, one 9 cm in length and the other 13 cm in length) fitted with KBr windows. The gaseous compounds were introduced to the reactor by using a standard vacuum manifold equipped with pressure transducers. The reactor accommodated copper sheets that were positioned on its bottom.

The progress of the LPHP of both organometallics was monitored by FTIR spectroscopy (a Nicolet Impact spectrometer) using absorption bands at 532 cm^{-1} ($(CH_3)_2Te$) and 828 and 1142 cm^{-1} ($(CH_3)_4Ge$), and also by gas chromatography (a Shimadzu 14A chromatograph) and gas chromatography–mass spectrometry (a Shimadzu QP 1000 mass spectrometer) using 2 m long Porapak P columns, programmed temperature (30–150 °C) and sampling by a gas-tight syringe. The chromatograph was equipped with a flame-ionization detector and coupled with a Shimadzu CR 5A data processor. Gaseous products were identified through their mass spectra.

After the irradiation and the deposition of solid films, the reactor was evacuated and the metal sheets were transferred for the measurements of their properties by Raman, X-ray photoelectron spectroscopy (XPS) and by electron microscopy.

The Raman spectra of the films on copper substrate were measured on a Renishaw (Ramascope model 1000) Raman microscope coupled with a CCD detector. The exciting beam of an argon-ion laser was defocused to obtain an energy density in the range 4×10^2–4×10^4 W cm^{-2}.

The XPS spectra of the deposits were measured using an ESCA 310 (Gammadata Scienta) electron spectrometer equipped with an aluminium Kα X-ray source and hemispherical electron analyser. The measurements were performed in a vacuum of 10^{-7} Pa. The spectra of Ge 3d, Te 3d and C 1s electrons were recorded. The curve fitting of high-resolution spectra was accomplished using a Gaussian–Lorentzian line shape and a damped nonlinear least-squares procedure.

The transmission electron microscopy (TEM) and electron diffraction (ED) experiments were performed in a Philips CM-200 microscope with a supertwin objective lens, working at 200 kV with an LaB_6 filament and ±45° tilt side-entry specimen holder (point resolution: 0.24 nm). The instrument is equipped with an EDAX detector for chemical analysis. The samples for the TEM observation were prepared by forming a suspension in ethanol of the powder obtained by scraping off the metal sheets. Some drops were suspended in a holey carbon grid.

$(CH_3)_4Ge$ (Aldrich, 98% purity) and $(CH_3)_2Te$ (prepared after a literature procedure,[29] 95% purity) were distilled prior to use.

RESULTS AND DISCUSSION

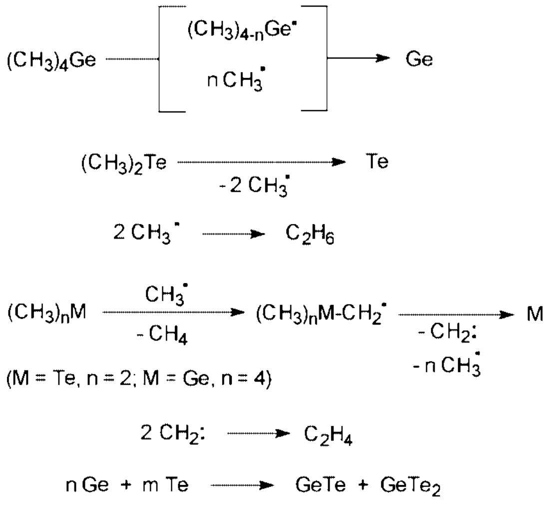
The TEA CO_2 laser irradiation of the gaseous $(CH_3)_4Ge$–$(CH_3)_2Te$–SF_6 mixtures results in the formation of ethane, methane, ethene and propane, and concomitant deposition of black solid films that coat the reactor surface near the entrance window. The relative molar amounts of the hydrocarbons (ethane (53–57%), methane (24–29%), ethene (13–16%), propane (3%)) are similar to those observed in the LPHP of $(CH_3)_2Te$[30] and in the LPHP of $(CH_3)_4Ge$,[31] which were shown to yield elemental tellurium and germanium.

It is conceivable[30–32] that both homogeneous decompositions occur as a sequence of splits of the M–C (M=Te, Ge) bonds. These steps are followed by (i) combination of CH_3 radicals to ethane and (ii) [H]-abstraction by $CH_3^\bullet$ radical from the initial compound. The latter step leads to formation of $^\bullet CH_2M(CH_3)_n$ radical, which presumably decomposes into methylene, M and methyl radical ($^\bullet CH_2M(CH_3)_n \rightarrow M + :CH_2 + CH_3^\bullet$). All the reactions furnish the gas phase with tellurium and germanium atoms that could form clusters and react to GeTe and $GeTe_2$ (Scheme 1).

The irradiation conditions selected allow the formation of almost identical amounts of germanium and tellurium in the gas phase: the absorption of 400 pulses in the mixture with excess of $(CH_3)_4Ge$ causes depletion of 13–15% (ca 0.56 kPa) of $(CH_3)_4Ge$ and 75–85% (0.53–0.60 kPa) of $(CH_3)_2Te$.

We note that the presumed reaction between germanium and tellurium atoms/clusters is facilitated by their small size and by negative heat of GeTe formation. We also note that the irradiation conditions (high temperature gradients[23–25] in a limited volume of the gas phase) enhance the reaction between germanium and tellurium, as well as the crystallization of all species present.

The deposited films do not adhere to the metal substrate on the reactor walls and can be removed from these surfaces as an ultra-fine powder.



Scheme 1.

The visible Raman spectrum of the coating shows a broader band at 133 cm^{-1} assignable to Ge–Te bond mode in GeTe ($\Gamma1$ phonon mode[33] at 140 cm^{-1}) or $GeTe_2$[34,35] (A_1 mode[36] of $GeTe_4$ tetrahedral unit at 125 cm^{-1}). Neither a couple of sharp bands at 120 cm^{-1} and 140 cm^{-1} (respectively due[34] to the A_1 and E modes in crystalline tellurium), nor bands at 275 cm^{-1} (a Ge–Ge vibrational mode) and at 150 cm^{-1} (a Te–Te vibrational mode) characteristic of amorphous Ge_xTe_{1-x} glasses[37] were detected.

TEM images reveal the presence of nanostructured materials and show small bodies of about 30 nm agglomerated into chain structures (Fig. 1). The ED analysis of different selected regions shows both diffuse bands of an amorphous phase and single-crystal patterns. Different patterns for the selected areas indicate different proportions of amorphous and crystalline phases in different regions of the deposit. In general, the majority of the rings could be indexed[38] as GeTe and tellurium phases. A representative result of the ED experiments (Fig. 2) shows that all the rings could be indexed as GeTe (JCPDS card: 47–1079, *R*3*m* space group) and tellurium (JCPDS card: 36–1452, $P312_1$ space group) phases. However, some *d*-spacings corresponding to germanium (JCPDS card: 4–545, *Fd*3*m* space group) phase were found in other crystals. The fits to interlayer distances of crystalline GeTe (and also germanium and tellurium phases) reveal that the three constituents are not equally distributed in the deposit.

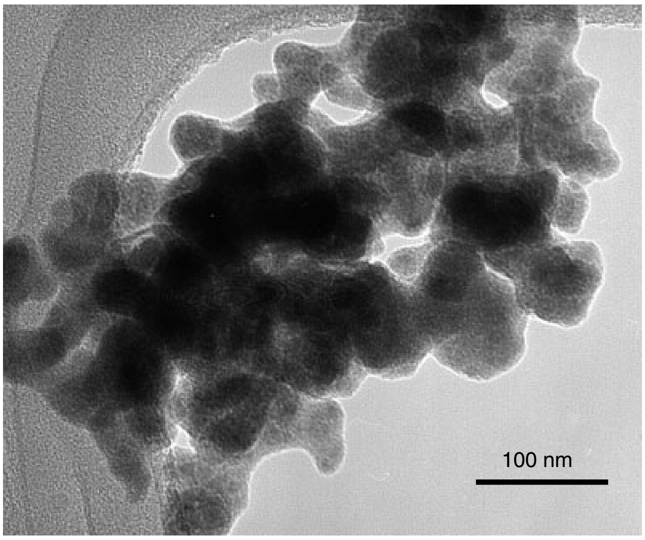


Figure 1. TEM image of the deposit.

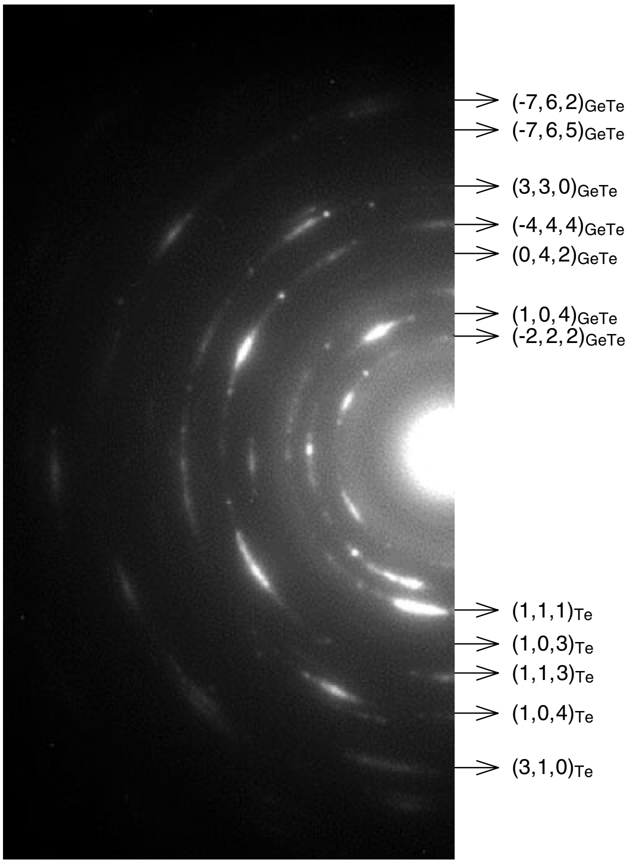


Figure 2. ED pattern corresponding to GeTe powder.

It is known that a binary Ge_xTe_{1-x} system easily takes a glass (amorphous) structure and also forms a stable crystalline GeTe (a rhombohedral α-GeTe,[39] a cubic β-GeTe[39,40] and a rhombic γ-GeTe[41,42]). Less-stable stoichiometries are described as $GeTe_4$[43] and a metastable $GeTe_2$[34,35,44] form. The latter undergoes disproportionation $GeTe_2 \rightarrow GeTe + Ge$, and its stability increases with increasing film thickness.[35]

All these species might be formed during the laser pulse. We assume that the reaction between the tellurium and germanium clusters takes place inside the hot laser zone (characterized by the temperature gradients[25]) at different temperatures within several microseconds. These conditions are feasible only for a very fast crystal growth. Furthermore, the crystalline and amorphous particles produced in different parts of the hot zone experience very fast cooling after the

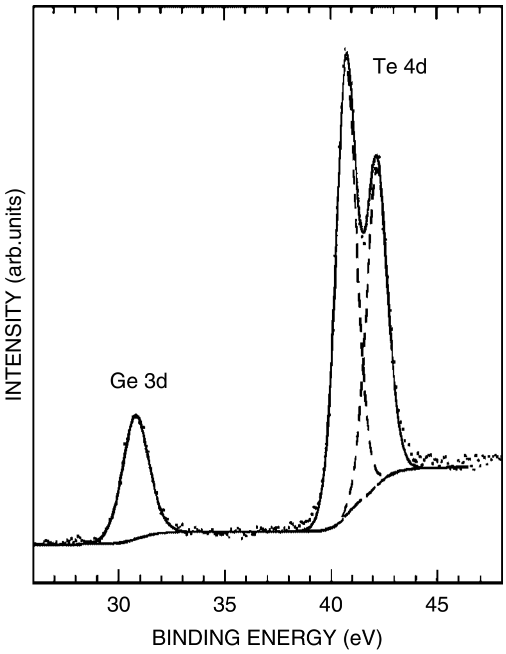


Figure 3. Fitted photoelectron spectra of Ge 3d and Te $4d_{5/2}$ electrons in the deposit.

laser pulse ceases. We assume that these specific conditions favour the formation of the crystalline GeTe form and are not suitable for yielding the crystalline $GeTe_2$ form.

The XPS analysis of the superficial layers of the deposit on copper (Fig. 3) is in keeping with the occurrence of GeTe. The separation of the Te $4d_{5/2}$ and Ge 3d lines amounts to 9.93 eV and is consistent[45,46] with that reported for GeTe (10.1 eV) but not for the elemental germanium and tellurium (10.9 ± 0.1 eV). This assignment is further supported by the value of the modified Auger parameter obtained: for the deposit it amounts to α' ($3d_{5/2}$, $M_4N_{45}N_{45}$) = 1063.0 eV, which is different to that[47] for elemental tellurium (α' ($3d_{5/2}$, $M_4N_{45}N_{45}$) = 1065.1 eV). The photoemission lines of tellurium are narrow and do not show the presence of two or more components. The atomic Ge/Te ratio, being 0.48, suggests that the $GeTe_2$ compound dominates in the topmost layers. The spin–orbit splitting of the Ge 3d spectrum is not observed, thus indicating the likely presence of an amorphous phase of the telluride.[46]

All the analytical data on the solid deposit thus unambiguously confirm the presence of nanosized crystalline GeTe and of amorphous $GeTe_2$ and prove the occurrence of the gas-phase reaction between germanium and tellurium clusters.

The results support further studies on the LPHP technique for synthesis of nanoparticles of other IV–VI and II–VI semiconductors in the gas phase.

Acknowledgements

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