Mendeleev Commun., 2003, 13(6), 251–252

Micro-Raman study of the solid products of thermal decomposition of tetraalkylgermanes

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10.1070/MC2003v013n06ABEH001822

The Raman study of whiskers formed as a result of thermal decomposition of tetraalkylgermanes demonstrated that the whiskers consist of single-crystalline germanium in a cubic modification coated with a thin carbon film of the diamond-like carbon (DLC) type.

The deposition of inorganic coatings and films from a vapour phase upon the decomposition of organometallics (MO CVD processes) is of great interest for modern electronics.[1] For instance, recently,[2] a plasma-chemical CVD process of Me_4Ge decomposition was reported to lead to the formation of semiconductive carbon–germanium films.

Systematic studies of the thermal decomposition of organogermanium compounds were started[3] as early as 1969 and continued in more recent years.[1,4,5] X-ray diffraction analysis and transmission electron microscopy (TEM) showed that the thermal decomposition leads to the formation of a solid Ge+C system in various morphological forms; a possible formation mechanism was considered in detail.[1,4,5]

In particular, at the terminal stage of the process, so-called whiskers (filamentary crystals) are formed. They consist of Ge+C and can be amorphous, polycrystalline or single-crystalline structures. They form complex morphological objects of the fractal type,[6] like needles with axial defects, thin bars with laterals, 'trees', 'vessels', *etc*. It was shown by TEM that most of the objects mentioned possessed carbon 'shells'.[4] When the process was completed and the ultimate solid-phase structure was built, carbon migrated to the surface and formed a continuous film covering the Ge-containing body. This is obviously due to the inability of germanium to form stable carbides. Note that this shell could exhibit different compositions and structures at the intermediate and ultimate stages of the process.

Laser micro-Raman spectroscopy is one of the best nondestructive methods for the identification of various carbon modifications since each of the latter exhibits its own characteristic Raman pattern.[7–9] The aim of this work was to apply this technique to elucidate the composition, structure and spatial arrangement of the solid products of tetraalkylgermane thermal decomposition. In particular, it was of interest to find out the way of carbon distribution in this system and the type of modification of carbon (the formation of fullerene-like structures and nanotubes was conceivable).

Et_4Ge and Bu^n_4Ge were taken as starting compounds. The experimental installation for carrying out the thermal decomposition was described elsewhere.[4] The deposition of needle-shaped Ge crystals was accomplished in a closed system on a heated Nichrome wire at a pressure of 0.01–0.05 Torr and a substrate temperature of 450–500 °C. In the gaseous products of R_4Ge thermal decomposition, the following compounds were identified by gas chromatography: C_2H_6, C_2H_4, n-C_4H_{10}, and H_2 for R = Et, and n-C_4H_{10}, n-C_4H_8, C_2H_6, and H_2 for R = Bu^n.

Raman spectrometers of the last generation equipped with a highly sensitive cooled CCD detector and a microscope with a TV camera allow one to carry out 'micro-mapping' of the surface of solid samples and thin films with spatial resolution about several microns.[7] We registered the Raman spectra of the solid products mentioned on a Jobin-Yvon T64000 spectrometer which is a one of this kind. The 514.5 nm line of a 1 mW SP2020 Ar^+ laser was used for spectra excitation. The samples were thin whiskers of *ca.* 0.1–0.01 mm in diameter. An image of a whisker obtained by means of an optical microscope is presented in Figure 1(*a*),(*b*) (magnification degree 10× and 50×, respectively). The Raman spectra were recorded both for the lateral surfaces of the whiskers and for the chip butt-ends. The Raman spectra of the whisker butt-ends [Figure 2(*a*)] were found to exhibit only one very intense narrow line at 301 cm^{-1} with a half-width $\Delta\nu_{1/2} \approx 7$ cm^{-1}. This line is well-known[10] to correspond to the optical mode of the crystalline germanium in its cubic modification, space group O_h^7 ($Fd3m$). Note that the spectrum characteristic of amorphous Ge[11] is absent. This result refines the XRD data[4,5] and shows that pure highly ordered Ge is inside the whiskers. The Raman spectra of the lateral whisker surfaces [Figure 2(*b*)] also exhibit the line at 301 cm^{-1} due to crystalline Ge; however, this line has an asymmetric contour and its half-width increases up to 14 cm^{-1}, which could be caused by partial disorder in the sub-surface layer, as well as by an internal stress.[2] Besides this line, the spectra of whisker surfaces also contain two broadened overlapping bands with maxima at about 1350 and 1580 cm^{-1} ($\Delta\nu_{1/2} \approx$ 150–200 cm^{-1}]. According to published data,[8,9,12,13] such a Raman pattern is characteristic of synthetic carbon films, so-called diamond-like carbon. The micromapping of the whisker surface, that is, surface scanning per-

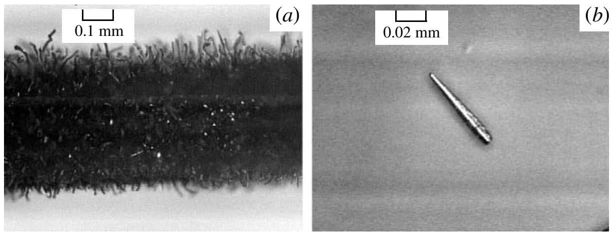

Figure 1 Images of (*a*) the test whisker under an optical microscope (magnification factor of 10) and (*b*) a small fragment slipped off from the surface of the whisker (magnification factor of 50).

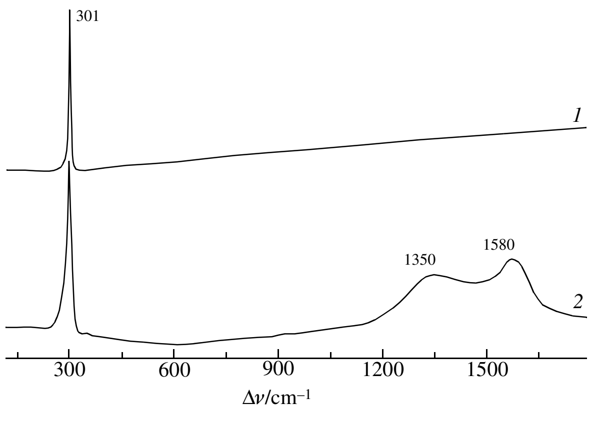

Figure 2 Raman spectra of (*1*) the butt-ends and (*2*) the lateral surfaces of the whiskers.

formed by the Raman method, points to the homogeneity and uniformity of the test carbon films. Neither carbon nanotubes (with their diagnostic Raman lines in the region 120–180 cm^{-1})[14] nor fullerenes (with their characteristic Raman spectra)[15] were found. It is also important that no Raman features in the region 550–650 cm^{-1} were observed, pointing to the absence of Ge–C bonds.[16]

Thus, the Raman data indicate that the whiskers formed as a result of thermal decomposition of tetraalkylgermanes consist of single-crystalline germanium in a cubic modification coated with thin diamond-like carbon film. The MO CVD process of thermal decomposition of tetraalkylgermanes proceeds *via* the separation of germanium and carbon phases with a germanium phase being forcedly incapsulated in thin carbon 'shells'. An analogous segregation of Ge and C in distinct domains was noted[17] for the the carbon–germanium films deposited by joint dc magnetron sputtering of germanium and graphite.

It is pertinent to mention here the data obtained by us upon investigation of the solid products of decomposition of dimethyl ether vapours under laser illumination.[18] In the latter case, the whisker studied was highly ordered crystalline graphite coated also with a DLC film.

This work was supported by the Russian Foundation for Basic Research (grant no. 01-03-33057), grant nos. NSh 1652.2003.3 and 1765.2003.3 and ISTC (grant no. 2511).

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Received: 3rd July 2003; Com. 03/2148