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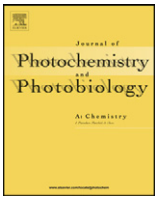

Laser ablation of Ga in dielectric breakdown of gaseous hydrocarbons: deposition of ambient-pressure unstable Ga nanophases in carbonaceous environment

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ABSTRACT

IR laser-irradiation of Ga in gaseous hydrocarbon (benzene, ethyne or n-hexane) results in ablation of Ga and adjacent dielectric breakdown (DB) in gaseous hydrocarbons. These processes lead to chemical vapor deposition of Ga nanoparticles-containing carbonaceous films. Volatile products of DB were examined by FTIR spectroscopy and GC and GC/MS techniques and revealed as arising from carbonization reactions in the gas phase. The solid products were analyzed by FTIR, X-ray photoelectron and Raman spectroscopy and electron microscopy and disclosed as Ga nanophases enveloped by graphite-like shell of carbonaceous phase. These nanophases include ambient pressure stable orthorhombic and amorphous structures and tetragonal, cubic and rhombohedral structures that have been previously observed only at high pressures. The reported procedure of chemical vapor deposition of the high-pressure Ga nanostructures thus represents a novel approach to these phases.

1. Introduction

There is a continuing interest in elemental gallium due to its potential applications as nano liquid-metal coolant [1], carbon nanothermometer [2], gallium-metal nanocomposites and nanostructured films for plasmonic applications [3,4], molten solvent for bulk synthesis of silicon nanowires [5] and multiwall carbon nanotubes [6], large droplets for catalytic growth of silica nanowire bunches [7] and nanoparticles for surface-enhanced Raman spectroscopy [8].

The fabrication of separated Ga nanoforms is rather difficult owing to the low melting point of Ga (29.8 °C) which makes coalescence to larger aggregates an easy process. Up to now, nanoparticles of liquid Ga have been grown by molecular beam epitaxy on sapphire [8,9] and GaN [10] substrates, liquid Ga nano-columns were prepared by heating GaN in a flow of ethyne [6] or by high-temperature reaction between Ga and methane [11], nanolayers of Ga were formed through nanoscale grain boundary penetration of Ga drop on Al film [3,4] and ordered nanostructures and nanoislands were fabricated by deposition of collimated atomic beam [12].

We have recently explored IR laser-induced metal (Co, Ni, Ag) ablation in dielectric breakdown of gaseous hydrocarbons [13–15]. The short IR laser pulses allow hydrocarbon carbonization in the plume of ablated metal particles within a temperature jump and subsequent stabilization of hot nanosized metal species by a fast (post-pulse) decrease in temperature and excess of simultaneously produced and deposited nanostructured carbon phase. The technique is suitable for fabrication of nanosized metal particles isolated in carbonaceous phase and shows a potential for synthesis of metastable nanostructures [15]. In a conjunction with our previous studies we now report on IR laser ablation of gallium in dielectric breakdown of several hydrocarbons and reveal that this process allows gas-phase deposition of nanostructured carbonaceous films containing Ga orthorhombic structures stable at ambient pressure and Ga tetragonal, cubic and rhombohedral structures that have been previously observed only at high pressures.

2. Experimental

IR-laser irradiation experiments were conducted in a Pyrex reactor (70 mL in volume) in the presence of 1 and 10 Torr of ethyne, benzene or n-hexane. The hydrocarbons were irradiated by a pulsed TEA CO_2 laser (model 1300 M, Plovdiv University) operating with a frequency of 1 Hz on the P(20) line of the 00^01-10^00 transition (944.19 cm^{-1}) and a pulse energy of 1.8 J. This radiation was focused with a NaCl lens (focal length 15 cm) on the Ga target positioned

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in the centre of the reactor above which were accommodated copper substrates. The pulsed irradiation of Ga in the hydrocarbons took place at the reactor temperature below 20 ° C and resulted in Ga ablation and decomposition of the hydrocarbon, both of which allowed deposition of Ga/C films on the Cu substrate and on the irradiated Ga target.

The reactor was described elsewhere [15]) and it was a tube fitted at each end with KBr windows and having a port with rubber septum enabling GC and GC/MS analyses of gaseous content and a PTFE valve connecting to vacuum manifold and pressure transducer.

The progress of the hydrocarbons decomposition and volatile decomposition products were analyzed directly in the reactor by FTIR spectrometry (an FTIR Nicolet Impact spectrometer, resolution 4 cm^{-1}) using diagnostic absorption bands at 1037 cm^{-1} (benzene), 3268 cm^{-1} (ethyne) and 1465 cm^{-1} (n-hexane). Aliquots of the irradiated reactor content were sampled by a gas-tight syringe and analyzed by gas chromatography-mass spectroscopy (a Shimadzu QP 5050 mass spectrometer, 50-m Porabond capillary column, programmed temperature 30–200 °C). The decomposition products were identified through their FTIR spectral diagnostic bands (C_2H_2, 731 cm^{-1}; C_4H_2, 628 cm^{-1}; CH_4, 1305 and 3016 cm^{-1}) and through their mass spectra using the NIST library.

The deposited films were analyzed with the FTIR Nicolet Impact spectrometer, a Nicolet Almega XR Raman spectrometer (resolution 2 cm^{-1}, excitation wavelength 473 nm and power 10 mW) and by electron microscopy (a Philips XL30 CP scanning electron microscope equipped with an energy-dispersive analyzer EDAX DX-4 of X-ray radiation) and a JEOL JEM 3010 microscope operating at 300 kV and equipped with an EDS detector (INCA/Oxford) and CCD Gatan (Digital Micrograph software). The Raman spectral analysis was carried out on different microregions of the films to verify the absence of non-homogeneous spots of the films on Cu substrate and to detect differences in the spectra for the film areas near the target crater. The transmission electron analysis was carried out on ground samples that were subsequently dispersed in ethanol followed by application of a drop of a diluted suspension on a Ni grid. Diffraction patterns were measured with a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube (Co Ka radiation, 40 kV, 30 mA, point focus), an X-ray monocapillary with diameter of 0.1 mm, and a multichannel detector X'Celerator with an anti-scatter shield.

Benzene (Lachema, purity better than 99.7 per cent), ethyne (Linde, purity better than 98,5 per cent) and n-hexane (Lach-Ner, purity better than 99 per cent) were evaporated from the liquid nitrogen-solidified compounds on a vacuum line prior to use.

3. Results and Discussion

The TEA CO_2 laser irradiation of Ga target in the presence of gaseous hydrocarbons (1 and 10 Torr of benzene, ethyne or n-hexane) results in a visible luminescence (plume), decomposition of the hydrocarbons and deposition of Ga/C films on the Cu substrate (and the nearby reactor surface) and on the irradiated target.

The films deposited by repetitive laser pulses on the Cu substrate are noticeably thicker than those deposited on the Ga target, because a substantial fraction of the film deposited in the region of the laser plume is repeatedly removed by next pulses.

Volatile products of the decomposition of benzene are ethyne (~ 60 mole %), ethene (~ 20-24 mole %), butadiyne (~ 10 mole %) and propane, 1-buten-3-yne, C_3H_4, and ethynylbenzene (each 0.1-0.5 mole %). The products of the decomposition of ethyne are butadiyne (90-96 mole %) and C_3H_4 and 1,3-butadiene (each 2-4 mole %). The products of the decomposition of n-hexane are ethyne (64 mole %), ethene (15 mole %), methane and butadiyne (each 5-6%), ethane and propene, each 2-3 mole %) and propane, propadiene, propyne, butane and 1,3-butadiene (each 0.2-1.2 mole %). These compounds were also formed in the pyrolysis of benzene [16], ethyne [17,18] and n-hexane [19,20] and are in line with carbonization of the hydrocarbons.

The solid films deposited on Cu substrate from benzene and ethyne with 40 pulses (1 Torr) and 100 pulses (10 Torr) were black, whereas those deposited at the same conditions from n-hexane were very thin and slightly darker than the original colour of the Cu substrate. The SEM-EDX analysis of the films deposited from

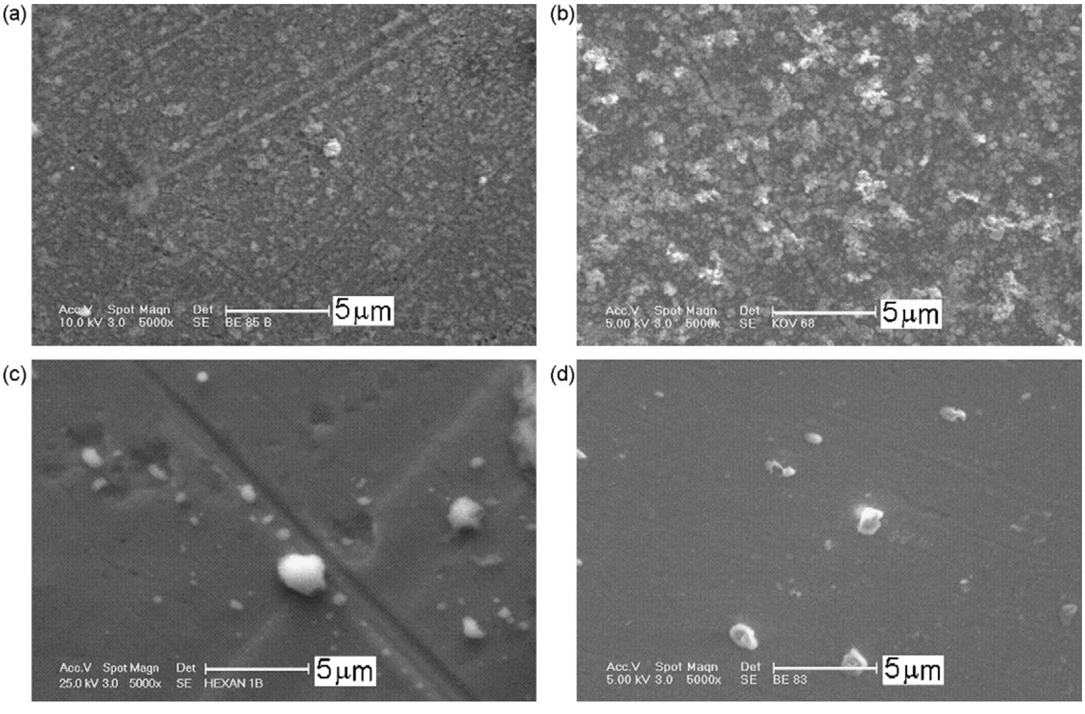

Fig. 1. SEM images of films deposited on Cu substrate from 10 Torr of benzene (a), ethyne (b), n-hexane (c) and 1 Torr of benzene (d).