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Laser-induced carbon deposition from supercritical benzene

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Abstract

A catalyst-free deposition of carbon onto a Si substrate immersed into benzene under supercritical pressure and temperature is induced by radiation of a Cu vapor laser. Raman analysis shows the signal typical of that for glassy carbon with a broadened D-peak. HRTEM indicates that the carbonaceous species have the shape of hollow rolls of 3–5 nm in diameter with multilayered walls with interlayer distance of 0.9 nm. The remaining liquid shows a strong luminescence in the visible, which is tentatively attributed to formation of polyaromatic compounds. © 2000 Elsevier Science B.V. All rights reserved.

Carbon deposition has attracted significant attention during the last decade due to large variety of its allotropic modifications, such as fullerenes [1], carbon nanotubes [2], onion-like structures, etc. Various techniques have been applied to decompose carbon-containing compounds, either with or without catalyst, such as arc discharge between graphite electrodes, laser ablation, chemical vapor deposition, to mention a few. Our previous studies on laser decomposition of hydrocarbons were focused on laser pyrolysis of aromatic compounds, such as benzene, toluene, or cumene, at the solid–liquid interface [3]. These compounds have the lowest energy of decomposition compared to other hydrocarbons. At ambient pressure, the carbon deposited on a Si substrate from liquid benzene is a glassy carbon with well-defined D and G peaks in the Raman spectrum [3]. Unlike a pure liquid benzene [4], the decomposition is believed to be a thermal process. The decomposition of the liquid hydrocarbon starts in laser-irradiated area of a Si wafer immersed into the liquid at the estimated peak temperature of the wafer of 800°C. As the irradiation proceeds, the liquid itself commences to absorb the laser radiation due to continuous generation of glassy carbon nanoparticles in the bulk. This means that the system demonstrates a positive feedback between the laser intensity and absorption. The calculations show that a carbon nanoparticle inside the laser beam is heated up to ca 1000°C during the laser pulse, which is quite sufficient to provide the decomposition of benzene around it. If the liquid benzene is exposed to laser radiation through a transparent solid (say, a reactor window), the products of its pyrolysis can be effectively quenched on the solid. This results in deposition of a diamond-like film on the transparent window with sp^3 fraction amounting to 80% [5,6]. The deposition of the diamond-like film proceeds from a gas bubble that expands in the vicinity of the interface solid–liquid. The bubble

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contains the mixture of benzene vapors and gaseous products of reaction [5], and the pressure in the bubble drops with its expansion from several kbars to ambient one.

One might expect new features of laser decomposition of aromatic hydrocarbons upon transition to supercritical conditions. In a sense, this process should be close to laser-induced chemical vapor deposition (LCVD), though the latter is carried out typically at low pressure of the precursor, up to 1 Torr. On the other hand, the critical pressure of benzene is about $p_{\mathrm{cr}} = 40$ atm at $T_{\mathrm{cr}} = 288°\mathrm{C}$, so that the density of the benzene molecules may greatly exceed that during the decomposition at ambient pressure. The elevated pressure may change the kinetics of aggregation of carbon clusters in laser-exposed area of the substrate compared to normal pressure conditions. High density of benzene and, eventually, of carbonaceous species in supercritical conditions is also characteristic for carbon deposition via ablation of a graphitic target with a high repetition rate ps laser [7], though the source of carbon in our case are the benzene molecules. In case of laser ablation, the resulting carbon consists of cluster-assembled carbon nanofoam. This Letter describes our preliminary results on morphological features of carbon deposited by laser pyrolysis of supercritical benzene.

A stainless steel cell with a glass window was filled with several cm^3 of liquid benzene of analytical purity. A single crystal Si wafer was placed on the bottom of the cell, the latter was heated from the bottom by the external heater. The temperature of the cell was controlled by a calibrated thermocouple. The beam of a copper vapor laser (wavelength of 510.6 nm, pulse duration of 20 ns, repetition rate of 10 kHz) was introduced into the cell through the glass window with a 10 cm focal distance lens. Typical laser fluence on a Si surface was 0.5 J/cm^2. To irradiate the extended area of the Si wafer, the cell was mounted on a computer-driven X–Y stage allowing its displacement under the laser beam with controlled scanning velocity in the range 0.3–3 mm/s. The samples of Si with deposited carbon were characterized by scanning electron microscopy (SEM), Raman spectroscopy, high-resolution electron microscopy (HRTEM). The luminescence of the remaining liquid was registered using a pulsed excitation at 532 nm.

Below the critical temperature, the medium in the cell is very inhomogeneous due to evaporation of the liquid and its condensation on the glass window as small drops. Upon further increase of temperature, the liquid passes through the stage of critical opalescence, and then the medium becomes quite transparent. No detectable decomposition of benzene is observed without laser irradiation at temperature 300–310°C during 2 h. We conclude that the possible catalytical action of steel walls of the cell on decomposition of the hydrocarbon can be neglected. The decomposition starts immediately upon laser exposure of the Si wafer. The observation of the process on a screen shows that decomposition of the hydrocarbon commences in the bulk of the cell after several minutes of the irradiation. This is due, undoubtedly, to the accumulation of carbon particles in the gas.

The carbon deposit on the Si wafer has an island-like structure (see Fig. 1). The lateral dimensions of each island are much smaller than the laser spot on the wafer (5–8 against 50 μm). The adherence of the deposit to Si surface is fairly good.

A significant amount of carbon is formed also in the bulk of the supercritical benzene. After

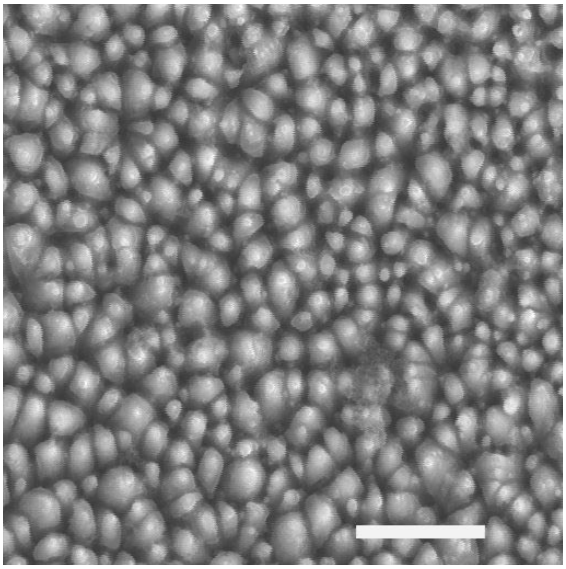

Fig. 1. SEM view of carbon deposit on Si. Scale bar denotes 20 μm.

cooling down of the cell, the remaining liquid contains the carbon suspension. The suspension decants in several hours and can be characterized by Raman spectroscopy and HRTEM.

Fig. 2 shows the HRTEM view of carbon formed in the cell. One can see carbon species that form a kind of rolls. They are empty inside, and their average diameter is 3–5 nm (Fig. 2a). The walls of the rolls are composed of several carbon layers. The measured interlayer distance is 0.9 nm in a wide range of laser fluences (Fig. 2b). To the best of our knowledge, this type of carbon structures has not been observed so far. At the same time, due to significant inhomogeneity of temperature inside the laser beam, the carbon residue shows another shape, in particular, of carbon filaments of hundreds nm long. The Raman signal also varies significantly over different portions of carbon. Some portions of carbon are Raman-silent, while the others are characteristic of glassy carbon. The latter spectrum shows that carbon deposited in supercritical conditions is more disordered than that observed by us previously during deposition from liquid benzene at atmospheric pressure in similar experimental conditions [3]. In particular, the D peak centered at 1310 cm^{-1} is significantly broadened, probably, due to the presence of other carbons. No Raman signal is observed in a low-shift domain, which should correspond to carbon planes with 0.9 nm spacing.

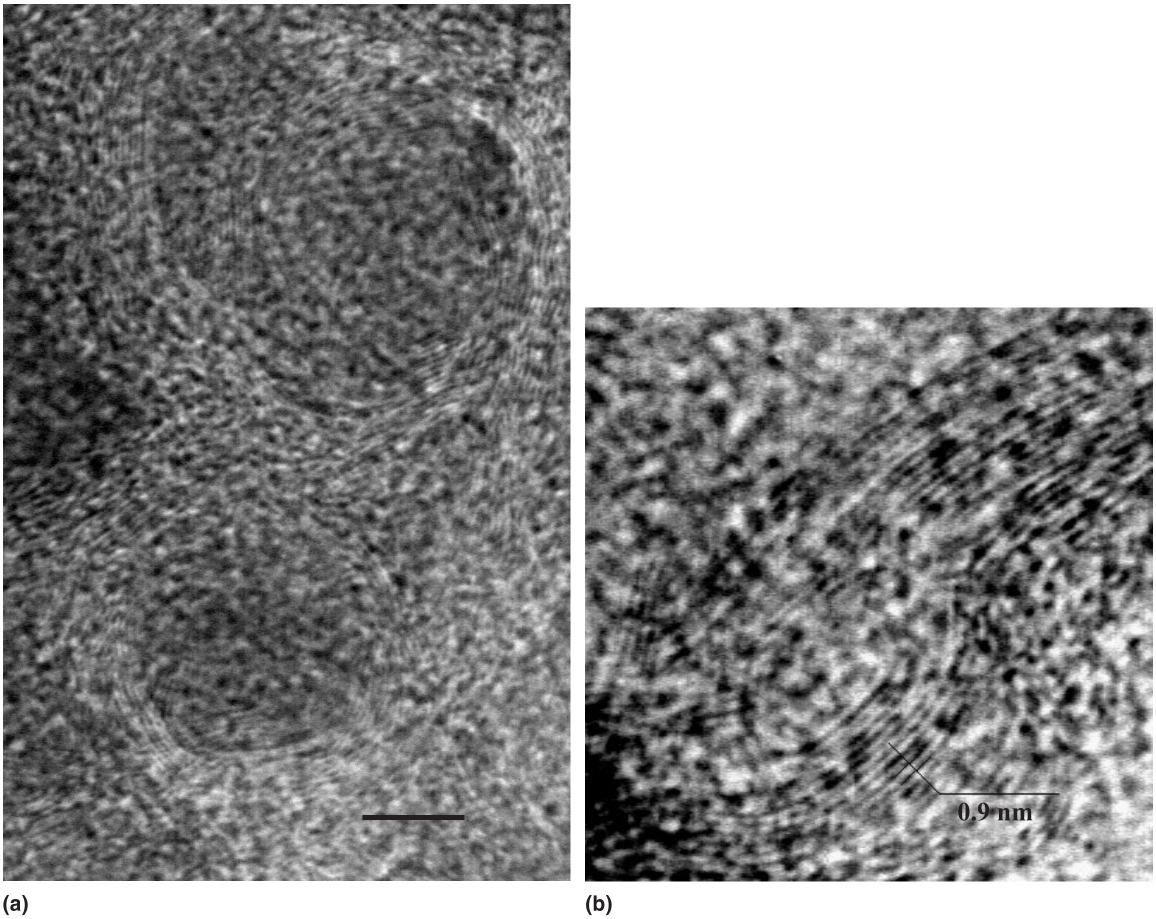

Fig. 2. HRTEM view of carbon rolls formed in the bulk of supercritical benzene upon laser irradiation. (a) Several rolls, space bar denotes 3 nm; (b) enlarged view of a roll, interlayer distance is 0.9 nm.

The peculiar feature of the deposition from benzene under supercritical conditions is the modification of the remaining liquid. Indeed, after the end of irradiation and cooling down, the remaining liquid shows a strong luminescence in the visible. The spectrum of luminescence is shown in Fig. 3. This spectrum is characteristic of dyes containing several aromatic dyes. Their formation might be attributed to high pressure and temperature in the laser beam. More information on the structure of the luminescent species can be obtained using the liquid phase chromatography, which is ongoing.

The specific carbon structures observed in the present work might be attributed to highly non-equilibrium conditions of laser-induced decomposition of supercritical benzene. The essential feature of the process is the high repetition rate of laser pulses, which favors the accumulation of carbon species in the medium. The decomposition of benzene starts on the Si surface, then the absorption of the gas increases with the time of irradiation. Small carbon particles become the centers of benzene decomposition. Indeed, the temperature T of the particle can be estimated using the following relation [5]:

$$T = \frac{Rjk_a}{4k_1 t_p},$$

where R stands for the particle radius, j is the laser fluence, k_1 the heat conductivity of the surrounding liquid, and t_p is the laser pulse duration. This expression is derived for the case when the particle radius R is much lower than the heat propagation length in the surrounding medium during the laser pulse of duration t_p: $R^2 \ll a_1 t_p$, where a_1 stands for the heat diffusivity of benzene. The term

$$k_a = \exp\left[-0.2\sqrt{n^2+k^2}-1\right] \times \left[1-\exp\left(-\frac{8\pi kR}{\lambda}\right)\right]$$

takes into account the decrease of the effective cross-section of the particle of radius $R \ll \lambda$ compared to its geometric cross-section. Here n and k stand for the refractive index and extinction coefficient of glassy carbon, respectively. At laser wavelength $\lambda = 510.6$ nm, for a bulk glassy carbon $n = 2$ and $k = 0.7$ [8]. For radius R of several nanometers the particle is heated to 1000 K at a laser fluence of 1 J/cm^2. This temperature rise is gained on the background temperature in the cell of 300°C. Thus, the overall temperature of the carbon particle is high enough to cause the decomposition of benzene molecules around the particle. The temperature of the gas inside the laser beam is essentially inhomogeneous, its maxima coincide with the absorbing carbon particles. The specific morphology of carbon presented in Fig. 2 might be due to vortex-like motion of carbon nanoparticles inside the laser beam. Indeed, the formation of gaseous products of benzene decomposition, mainly CH_4 and C_2H_2 [6] may induce the instability of gas flow around the carbon particle. This point, however, requires further studies. The high pressure around the absorbing carbon particle favors the formation of multi-ring compounds, as confirmed by strong luminescence of the remaining liquid.

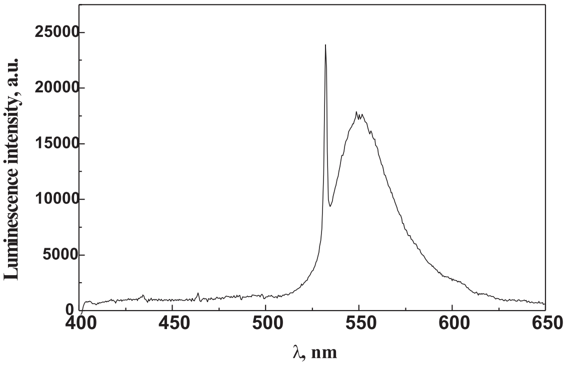

Fig. 3. Luminescence spectrum of the liquid remaining in the cell. The excitation wavelength is 532 nm. The sharp peak is due to scattered excitation light.

Thus, the characteristic feature of laser-assisted carbon deposition from supercritical benzene is the specific form of carbon presented as empty rolls of 3–5 nm in diameter. The walls of these rolls are made of several carbon planes with an interlayer distance of 0.9 nm. The decomposition of benzene in our experimental conditions seems to proceed via thermal heterogeneous reaction on a Si substrate in the first stages of irradiation and then on carbon nanoparticles in the bulk of gaseous benzene. The carbon deposited from supercritical benzene might possess interesting field emission properties, like carbon nanotubes or diamond-like carbon.

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