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Deposition diamond like carbon coating with a repetition rate pulsed CO2 laser

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Experimental studies of obtaining nanocarbon structures on the surface of various materials by laser deposition using a repetition rate pulsed CO_2 laser (peak pulse power of about 1.5 MW) are presented. Deposition of a diamond-like carbon layer on surfaces with high deposition rates is shown.

Keywords: Pulsed laser deposition (PLD), diamond-like carbon (DLC), Raman spectroscopy, plasma spectroscopy, repetition rate pulsed CO_2 laser.

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Introduction

High research and technology interest is currently shown in various applications of carbon nanostructures. This is associated with their unique physical properties (hardness, conductivity, strength, etc.). Applications of these structures (carbon CNT nanotubes, diamond-like coatings for improvement of properties and surface characteristics of various materials) are being studied extensively.

Laser vaporization of graphite is one physical methods used to produce carbon nanostructures [1,2]. This method ensures high process purity and does not require carbon source heating up to high temperature, however, the performance is not high, since the pulse lasers used for these processes (excimer and YAG) have moderate average power and energy per pulse.

Pulsed CO_2 lasers ensure high energies per emission pulse and be used with pulse repetition rates up to 1000 Hz. LAERT repetitively-pulsed laser (RPL) with emission pulse whose width is equal to several hundreds of microseconds and peak power is equal to several kilowatts was used to prepare complex compound nanopowders [3,4].

Application of diamond-like coatings to metals and optical components is a well developed carbon nanotechnology process. Various types of plasmatrons are used for this process. Industrial systems for diamond-like carbon (DLC) layer application have been developed [5].

For application of high quality DLC coatings, a sophisticated and long-term process is required using high-vacuum systems that perform surface cleaning by ion beams and deposition by gas-discharge (magnetron or high-frequency) sources. The process time is more than one hour.

For isotope separation, JSC GNTs RF TRINITI has developed and uses highly-reliable repetitively pulsed CO_2 lasers with high peak powers, energies per pulse equal to several joules and repetition rate more that 400 Hz, that can be operated continuously during several weeks. These lasers were used from 2000 to 2005 at the isotope separation factory in Kaliningrad [6].

High peak power of pulsed CO_2lasers can provide high carbon (graphite) evaporation rates without additional heating and a high vapor (plasma) temperature due to longwave emission absorption and, consequently, high cooling rates. The average power of these lasers is more than 1500 W to ensure high deposition process rates.

Experiments using such type of RPL were carried out to study whether such lasers may be used to apply diamond-like coatings.

1. Experimental setup description

The experiment setup is shown in Figure 1.

Multimode emission of the 1.2 J repetitively pulsed CO_2 laser with beam cross-section 3×3 cm was focused by the KCl lens with a focal distance of 26 cm and forwarded through a window made from the same material to the chamber with a volume of about 1 l. The chamber was pressurized by a fore-vacuum oil-free pump to 50 Pa and could be filled with inert gas.

Maximum laser pulse repitition rate was 200 Hz, but since the target did not move during the experiments, the work was carried out in the range of $1-20$ Hz. The experiments used a flat pyrographite target that could be placed at various distances from the lens focus. Polished polycore, molybdenum and nickel foil were used as deposition samples. These samples were pre-cleaned in ethanol. 2×3 cm samples were placed parallel to the target at distances from 3 mm to 13 mm.

Emission pulse waveform is shown in Figure 2. The pulse is typical for pulsed TEA CO_2 lasers and contain a short intense peak and long tail.

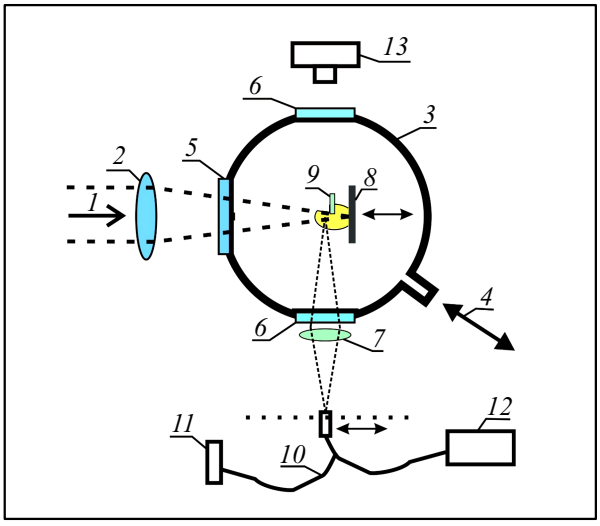

Figure 1. Experiment setup: *1* — laser beam, *2* — KCl lens, *3* — vacuum chamber, *4* — vacuum pump, *5* — KCl window, *6* — diagnostic windows, *7* — lens, *8* — target, *9* — sample, *10* — optical fiber, *11* — photodiode, *12* — spectrograph, *13* — photo camera.

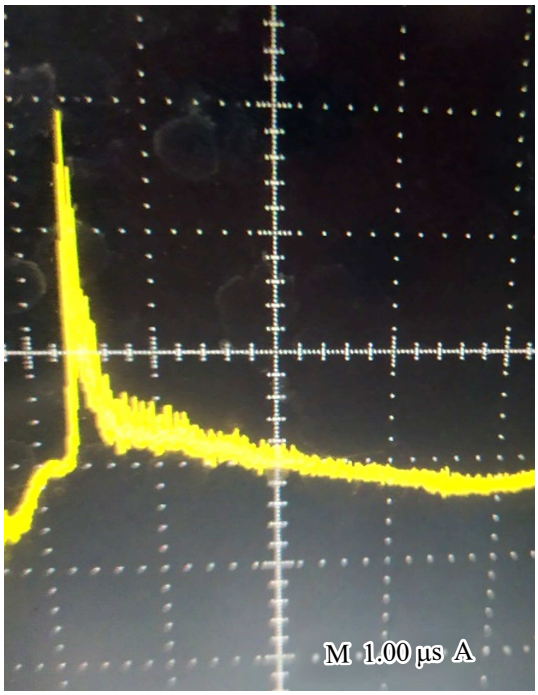

Figure 2. Emission pulse oscillograph record.

Peak width at base is 0.3 μs, full pulse width is about 3 μs. Peak emission power was 1.5 MW. Maximum emission power density at target in lens focus (by plastic print measurements) was equal to $6 \cdot 10^8$ W/cm^2.

Integral photography of plasma cloud was used for the experiments. For 3D spectral diagnostics of plasma, plasma image was projected using the lens to a 200 μm silica optical fiber end that could move in the image plane. The optical fiber had two output ends, one of them was connected to THORLABS CS100 compact spectrometer with a wavelength range from 300 to 700 nm. Spectral wavelength resolution of this instrument is 1.5 nm. The instrument was connected to PC for signal processing and storage. The second optical fiber end was connected to THORLABS PDA36A-EC diode photodetector connected to the oscilloscope for plasma glow recording.

2. Plasma characteristics

The experiments were carried out by target irradiation in vacuum at about 50 Pa. Figure 3 sjows integral photographs of the carbon plasma in vacuum with the target placed near the focus with various attenuation degrees by neutral filters.

These photographs show that the main heating of the evaporated carbon takes place near the target surface at a distance of approx. 3–5 mm, then spherical plasma expansion occurs. When pulsed lasers with a pulse width lower than tens of nanoseconds and wavelength shorter than 1 μm (solid-state or excimer) are used for deposition , the carbon plasma is spread in a form of expansion cone that is indicative of a merely evaporation process [7]. In our case, significant heating of the plasma occurs near the surface due to high absorption of 10 μm emission .

Figure 4 shows oscillograph records of a signal from the photodetector from a zone near the target surface (1) at 4 cm (2) from the target.

The assessment of these oscillograph records (comparison of intensity peak delays with discharge activation pulse in the laser) shows that the plasma expansion rate is about 15 km/s.

Figure 5 shows time-integral spectral patterns of plasma in vacuum in three plasma cloud points.

With distance from the target, C_2 (516 nm) bands prevail in this spectral region. Moreover, CN (388.3 nm) line is present in the spectrum near the target. This compound is probably formed in the presence of residual air in the chamber.

Plasma temperature was determined by the CN line using the procedure described in [8]; and is equal to about 6000 K.

Plasma emission spectra observations suggest that the sample surface shall be placed in the C_2 formation region to achieve the best diamond-like layer production conditions.

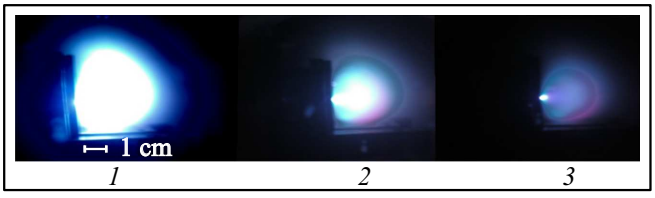

Figure 3. Carbon plasma photographs: *1* — without attenuation with a neutral filter (500 nm), *2* — x 2.5 attenuation, *3* — x 3.4 attenuation.

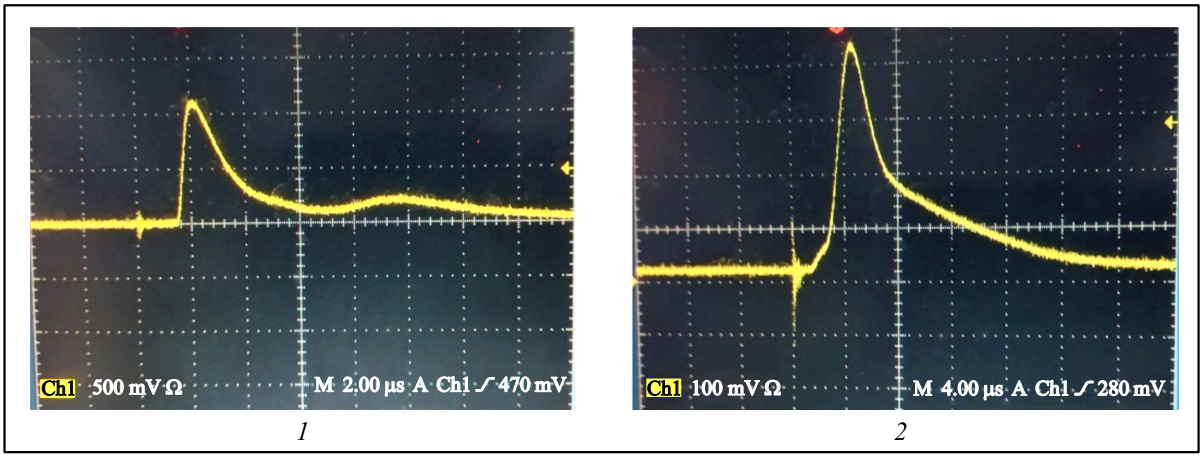

Figure 4. Oscillograph records of intensity signals from the photodetector: *1* — near the target, *2* — 4 cm from the target.

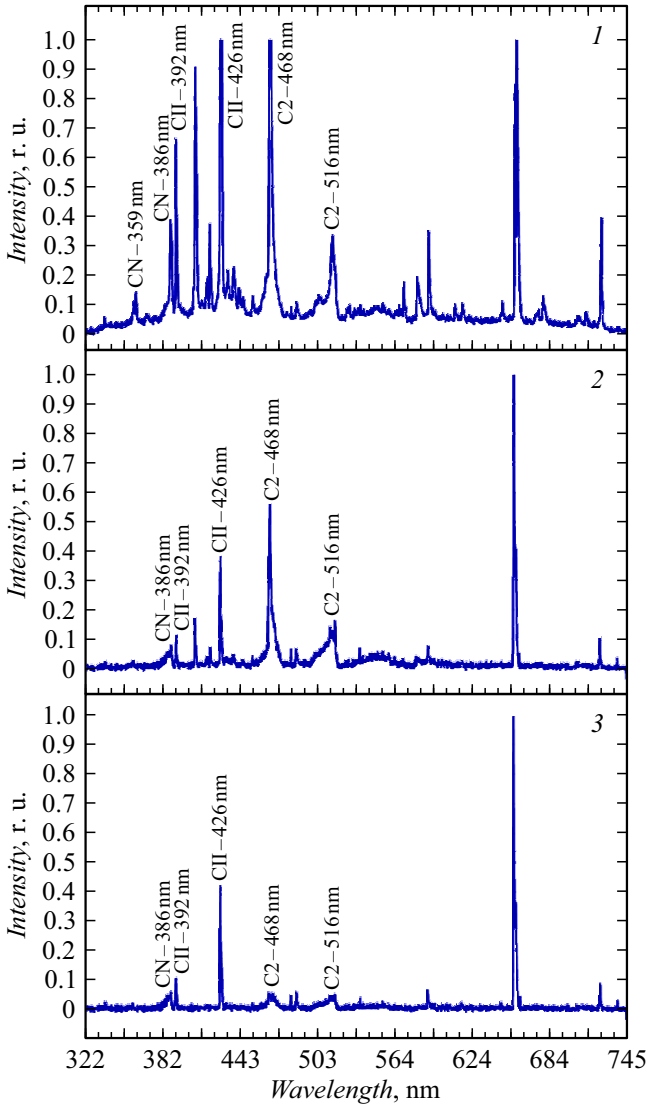

Figure 5. Carbon plasma spectra at several distances from the target surface: *1* — 3 mm, *2* — 15 mm, *3* — 18 mm.

3. Analysis of obtained coatings

Polycore and molybdenum were used as substrates. Deposition was carried out in vacuum at residual pressure about 50 Pa. The substrate was placed against a pyrographite target at a distance of 12 mm .

The coating composition was measured by the Raman-scattering spectroscopy method using Solar spectrometer (Republic of Belarus). 532 nm laser emission was used for spectra excitation. Figure 6, *a* shows the Raman spectrum of the vacuum deposited layer with dominating intensive wide asymmetric band in 1100−1700 cm^{-1} region with the peak near 1530 cm^{-1}. This spectrum is similar to the diamond-like carbon spectrum (in foreign literature known as DLC or ta-graphite) — sp^2- and sp^3 hybridized carbon with a large fraction of sp^3 bonds. Mathematical spectrum processing (deconvolution) (Figure 6, *b*) detects two bands: 1360 cm^{-1} (D band of graphite) and 1530 cm^{-1} (G band of graphite). G band shift to 1530 cm^{-1}, instead of 1580 cm^{-1} that is typical for graphite, may be due to the presence of a large fraction of sp^3 hybridized carbon [9].

Profilometer analysis of the polycore sample shown in Figure 7 demonstrates that the average thickness of the vacuum deposited layer is 0.9 μm. This measurement was made by 20 pulses sent to the pyrographite target. For comparison: the average coating deposition rate by IPCVD method is 7.4 nm/min [10], by PVD method is 0.1 μm/min [11]. In this case, at a repetition rate of 100 Hz, deposition time of a layer about 1 μm in thickness will be equal to 0.2 s. The „knocking-out“ rate required to knock out the carbon material from the target estimated by target weighing before and after irradiation was equal to 1.28 μg/impulse.

Deposited material surface quality was visually examined using Axia ChemiSEM (Thermo Scientific) scanning election microscope. Figure 8 shows the microphotograph of a sample with deposited carbon material. It shown that

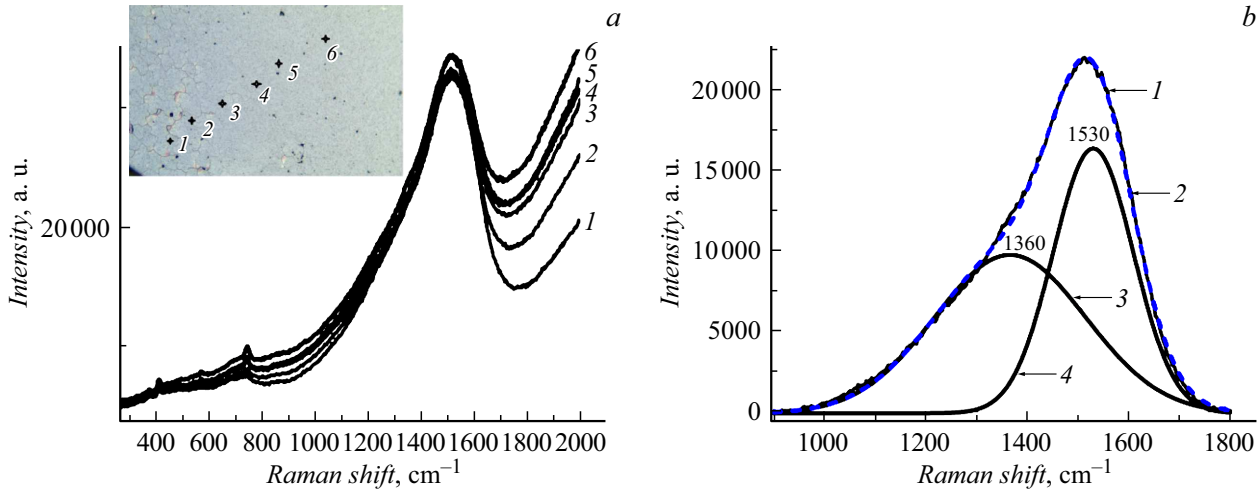

Figure 6. Raman spectrum of the surface layer deposited on the polycore substrate in vacuum: *a* — spectra recorded in various surface points; *b* — result after mathematical spectrum processing (deconvolution).

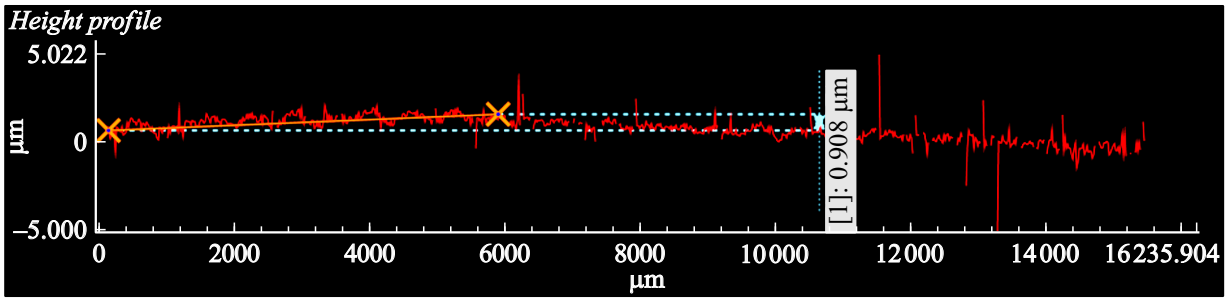

Figure 7. Surface profile cross-section of the test sample area measured using a fiber optic confocal profilometer

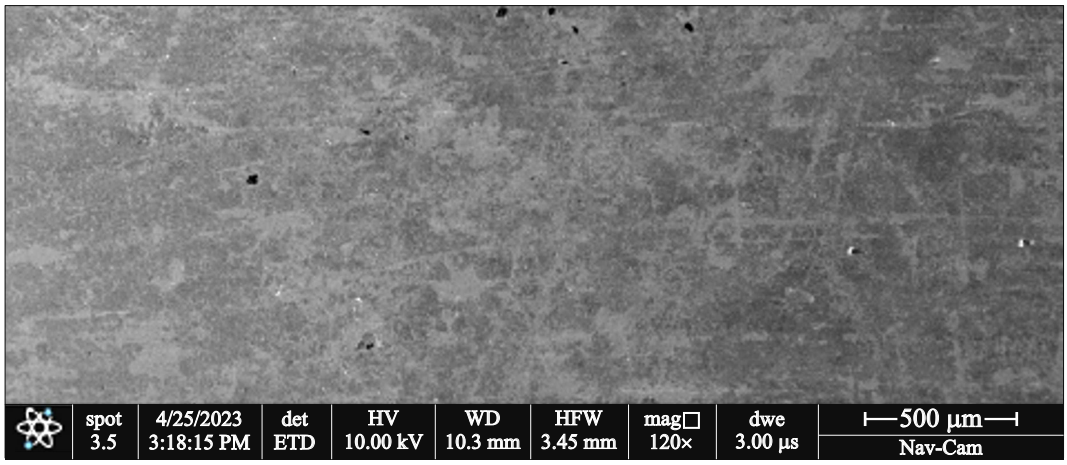

Figure 8. Microphotograph of the „molybdenum with vacuum deposition“ sample taken by ×120 scanning election microscope.

the major part of the coating is uniformly spread over the substrate surface and is free of defects.

Conclusion

Thus, it has been shown that diamond-like layers can be deposed at a high rate using repetitively-pulsedCO_2 lasers with high peak power. High peak emission power makes it possible to heat the plasma near the target surface up to high temperatures to ensure intense graphite evaporation. Since good adhesion of these layers with the substrate material is required for industrial applications, further investigations will be carried out in this area. Production processes using such lasers may be developed.

Conflict of interest

The authors declare that they have no conflict of interest.

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