Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 74 (7) 773–779 (2009)
JSCS–3875
UDC 66.088:546.26–162:531.728:53.086
Original scientific paper

Laser reflection spot as a pattern in a diamond coating – a microscopic study

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(Received 3 July 2008, revised 13 March 2009)

Abstract: Diamond coatings were deposited by the synchronous and coupled action of a hot filament CVD method and a pulsed CO_2 laser in spectro-absorbing and spectro-non-absorbing diamond precursor atmospheres. The obtained coatings were structured/patterned, *i.e.*, they were comprised of uncovered, bare locations. An extra effect observed only in the spectro-active diamond precursor atmosphere was the creation of another laser spot in the coating – a reflection spot. In order to establish the practical usability of the latter one, extensive microscopic investigations were performed with consideration of the morphology changes in the spot of the direct laser beam. Normal incidence SEM images of this spot showed a smooth surface, without any pulse radiation damage. AFM imaging revealed the actual surface condition and gave precise data on the surface characteristics.

Keywords: diamond coating; hot filament CVD; CO_2 laser; radiation reflection; SEM; AFM.

INTRODUCTION

A wealth of high-valuable technological properties of diamond has become fully available in thin film form by chemical vapour deposition (CVD). The hot filament chemical vapour deposition method (hfCVD) is a simple and inexpensive approach for obtaining good quality diamond films. The joint, synchronous action of a laser – the synergy – in the course of diamond coating deposition, enables a patterned coating to be obtained in a single-step procedure without any previous or subsequent processing. The main purpose of achieving the hot filament CVD-pulse CO_2 laser synergy in the synthesis of a diamond coating is to use the hot filament for the production of atomic hydrogen in sufficient quantities and the pulse CO_2 laser as a pattern-writing agent.

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doi: 10.2298/JSC0907773R

The synergy of the hot filament CVD method with a number of lasers operating in a broad spectral region was realised in order to obtain diamond coatings. Different lasers were used: excimer lasers ArF (193 nm)[1,2] and XeCl (308 nm);[1,3] an Ar-ion laser (514.5 nm);[4] a pulsed, frequency-doubled Nd:YAG laser (532 nm);[5,6] a continuous wave (cw) Nd:YAG laser (1064 nm);[7] a cw/pulsed CO_2 laser (10.6 μm)[8] and a pulsed CO_2 laser.[9] In all these cited works, except for two, the spectro-non-absorbing diamond precursor, CH_4 (1–3 %) in H_2 was used.

A spectro-absorbing diamond precursor atmosphere in the synergy laser–conventional CVD method takes advantage of another specific, important characteristic of laser radiation – monochromacity (in addition to high-directionality and high-intensity), which justifies the use of rather expensive/sophisticated instrument. In a spectro-absorbing diamond precursor atmosphere, the synergy of the hot filament CVD method with either an ultraviolet excimer laser[1] or an infrared-pulsed CO_2 laser[9] enables specific coating patterning – by deposition suppression, *i.e.*, impoverishment in irradiated locations. The obtaining of another laser spot in the coating, the reflection spot, indicated a possibility of exploiting the beneficial and avoiding the detrimental effects of pulse laser radiation. An SEM comparison of the spots created by the direct laser beam and by the reflected laser beam showed the absence of any substrate surface damage in the latter case. Microscopic investigations of the reflection spot down to the nano-scale were additionally undertaken in order to ascertain the substrate surface quality required for applications in diamond coating technologies.

EXPERIMENTAL

A reaction cell with a hot filament and a TEA pulsed CO_2 laser were set opposite to each other on the same optical axis, in order to accomplish their synergy. The reaction cell with the hot filament was coupled to a vacuum apparatus equipped with a pump, a pressure gauge and a gas flowmeter. The Ta filament (0.5 mm diameter) was supplied with electrical current from the a.c. mains through variable transformers. Molybdenum was chosen as the target/substrate in all synergy experiments, based on a study of different substrate materials for diamond CVD.[10] The Mo substrate (20 mm×10 mm×0.5 mm), mirror-polished by a standard metallographic procedure, unseeded, was mounted at a distance about 5 mm from the filament. The working parameters were as follows: substrate temperature ≈ 900 °C, filament temperature 2100–2200 °C, total working pressure 30 mbar, gas flow rate 50 cm^3 min^{-1}, experiment duration $t_{dep} = t_{irr} = 2.5$ h. Gaseous mixtures, C_2H_4 (0.5 %) in H_2, C_2H_4 (7.5 %) in H_2 and CH_4 (1 %) in H_2, were prepared before the experiments.

Radiation of the pulsed TEA CO_2 laser[11] was focused by a ZnSe lens (f = 25 cm) onto the Mo target/substrate mounted in the reaction cell at a distance from the filament of ≈ 1–2 mm. The laser working characteristics were as follows: pulse power (at a spike) 0.5 MW; pulse duration 120 ns (initial spike), ≈ 2 μs (pulse "tail"); repetition rate ≈ 3 Hz; output wavelength 10.6 μm; multimode working regime; spot size at the focus ≈ 1 mm^2; beam incidence angle to the surface 90°.

Characterisation of the resulting diamond coatings was performed by scanning electron microscopy (Jeol JSM 35, accelerating voltage 25 kV). The topography of the uncovered

substrate surface in the reflection spot was imaged by a powerful, high-resolution AFM instrument, Digital Nanoscope (Nanotec Electronica, Spain), working with WSxM software.[12]

RESULTS AND DISCUSSION

The diamond coating was deposited by the simultaneous action of the hot filament and the pulsed CO_2 laser from the spectro-absorbing diamond precursor atmosphere, C_2H_4 (0.5 %) in H_2. The obtained coating contained two laser spots situated in regions of reduced thickness. The first spot was created at the focus of the direct laser beam. Deposition impoverishment in the spot surrounding and moderation of the photothermal effect in the spot centre were explained by absorption of the laser beam in ethene.[9]

The second spot, made synchronously with the first one, is presented in the SEM micrographs shown in Figs. 1a–1d. The whole spot can be seen in Fig. 1a. A "patch deposit" gathered in the middle point of the spot is shown in Fig. 1b. The diffuse spot border and the gradual crystallites rarefaction indicate the influence of the spectro-active agent during the deposition, Fig. 1c. A detail from

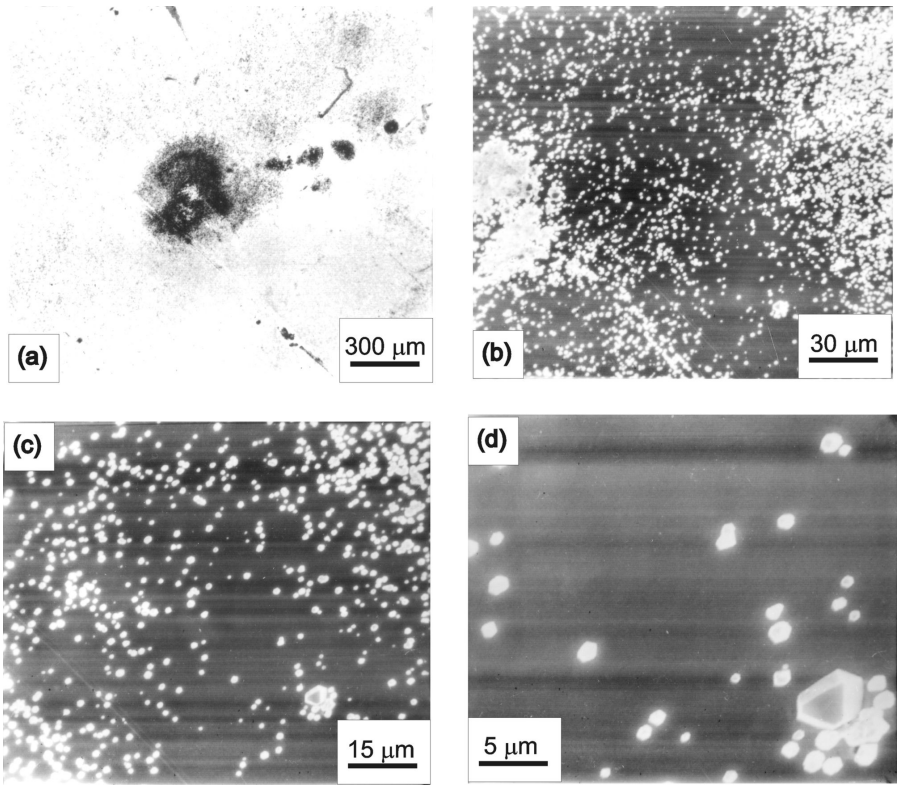

Fig. 1. Diamond coating of synergy obtained from C_2H_4 (0.5 %) in H_2: a) whole reflection spot; b) patch deposit in the central point of the spot; c) diffuse spot boundary; d) details from this spot.

the spot is shown in Fig. 1d. This spot resulted from specular reflection at the mirror-finished Mo substrate and backward reflection at the laser output coupler. It is well known that the reflectivity of metals increases with increasing incident radiation wavelength, and that for a CO_2 laser, the radiation reflectivity approaches unity (for molybdenum $R = 0.985$[13]). After specular reflection at the Mo substrate, the radiation reverted through the lens, become defocused after the focal point, *i.e.*, diverged, and reached the Ge output coupler* placed at an overfocus. At the coupler, the radiation is partly cast back, the straying rays travelled the same optical way, and then converged to create the reflection spot, and a cycle recurred until being extinguished by the absorbing medium. The speckle deposit in the spot centre, Figs. 1a and 1b, means that the laser radiation did not act at this point, which might indicate a possibility of a self-absorption effect of the laser radiation. On the other hand, deposition impoverishment in the spot stands just for action of the laser.[1,9] At the same time, the uncovered substrate surface in the spot without cracks produced by the pulse laser radiation, Figs. 1c and 1d, seemed as an acceptable/promising outcome of the laser action – a diamond coating pattern.

In order to compare laser modifications of the substrate surface effected in different working atmospheres, SEM micrographs (of the same/higher magnification) of the examined spot centres are given in Figs. 2a–2d. The modified substrate surface from the synergy experiment in the spectro-inactive diamond precursor atmosphere, CH_4 (1 %) in H_2 is presented in Fig. 2a. Figure 2b originnates from the spot made at the direct laser beam focus, and Fig. 2c stems from the reflection spot; both spots were created in the spectro-absorbing diamond precursor atmosphere, C_2H_4 (0.5 %) in H_2. The spot made at the laser beam focus in the highly concentrated diamond precursor atmosphere, C_2H_4 (7.5 %) in H_2 is shown in Fig. 2d. The effects of the laser radiation in the resulting coatings differ considerably: in the methane atmosphere, a laser radiation fluence of 15 J cm^{-2} produced the shown morphology pattern on the surface after removal of the diamond coating, Fig. 2a. In C_2H_4 (0.5 %) in H_2, the "palliated" surface morphology in the spot centre created at the direct laser beam focus, Fig. 2b, reveals damping of the laser radiation in the optically dense medium (simultaneously, the coating impoverishment in the spot surroundings confirms draining of the diamond precursor into a photolytic reaction channel), as has already been explained.[9] In the reflection spot, Fig. 2c, no cracks in the uncovered surface are visible; they might have vanished by radiation moving to and fro in the spectro-absorbing diamond precursor/medium. Only faint marks/traces of surface cracking seen in the spot centre created at the direct laser beam focus in C_2H_4 (7.5 %) in H_2, Fig. 2d, confirm the already noticed damping effect of the laser radiation in the

* Ge output coupler, transmission (declared): 20 %.

spectro-absorbing atmosphere.* These micrographs indicated the convenience of using the radiation reflection effect in the spectro-active diamond precursor in the studied synergy: diamond coating deposition with simultaneous patterning, without underlying surface damage to the substrate.

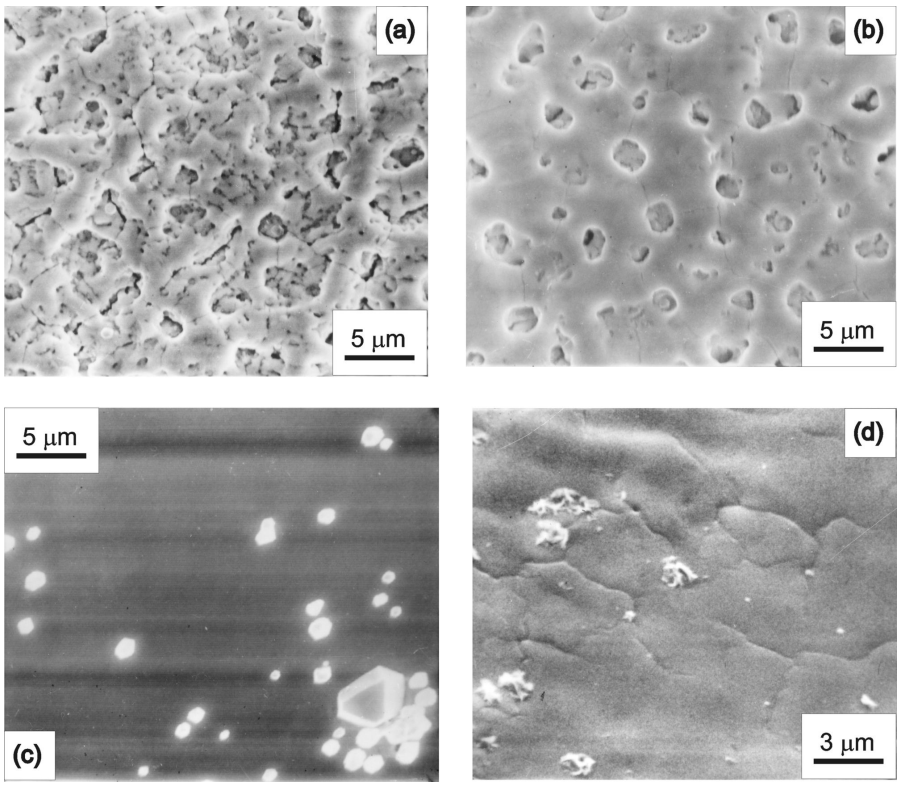

Fig. 2. Laser surface modifications/spots effected in different atmospheres during hfCVD-pulsed CO_2 laser synergy: a) spot created by the direct laser beam in CH_4 (1 %) in H_2; b) spot created by the direct laser beam in C_2H_4 (0.5 %) in H_2; c) spot created by the reflected laser beam in C_2H_4 (0.5 %) in H_2; d) spot created by the direct laser beam in C_2H_4 (7.5 %) in H_2.

Microscopic examination reaching even higher magnifications was undertaken in order to corroborate these findings. The morphology of the uncovered surface in the reflection spot is given by the AFM 3D-image (1.5 μm×1.5 μm) in Fig. 3a. Profile analysis of the examined surface segment, performed along the white, dashed line, is presented in Fig. 3b. The depth of the observed cracks (vertical distance between cursors) was ascertained in Fig. 3b, Graph (1), and equals

* Effect of the radiation reflection in the course of the hfCVD-pulsed CO_2 laser synergy was not observed in the spectro-unabsorbing precursor, CH_4 (1 %) in H_2, due to the formation of a thick diamond deposit; in the very high concentration of the spectro-absorbing diamond precursor atmosphere, C_2H_4 (7.5 %) in H_2, a reflection spot was not unambiguously discerned.

18 and 24 nm. The width of the observed cracks (horizontal distance between cursors), seen in Fig. 3b, Graph (2), amounts to 120 and 160 nm. The roughness of the examined surface segment is 7.5 nm (all numerical values are rounded). The presented evidence indicates that the pulsed laser radiation produced nanoscale surface damage in the reflection spot created in the micrometer-thick diamond coating. Consequently, applications which are unaffected by nanometric defects of the substrate surface are suitable for this method of coating patterning.

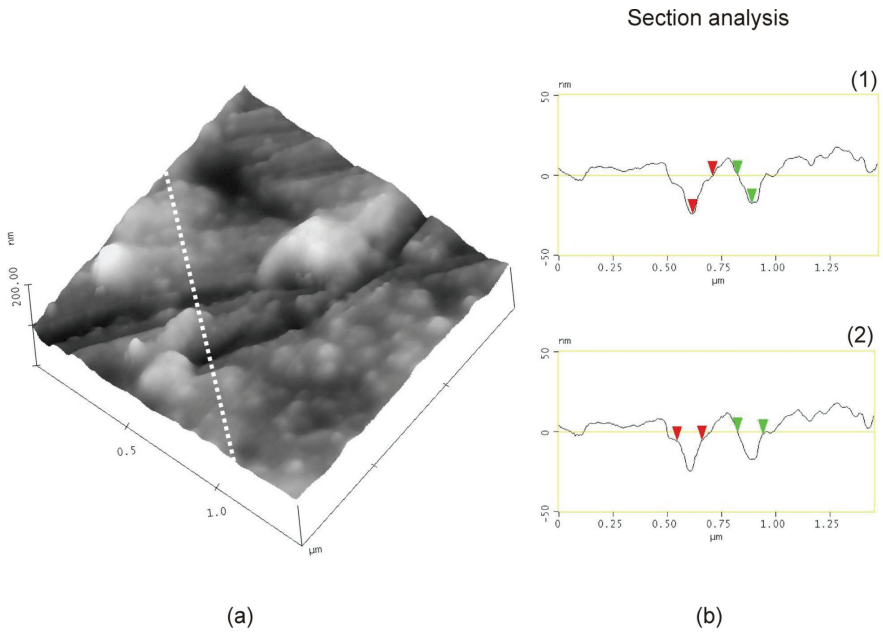

Fig. 3. Uncovered substrate surface in the reflection spot taken by AFM: a) 3D-surface view of the morphology (the white, dashed line indicates the location of the section analysis); b) profile of the section analysed, giving the depth (1) and width (2) of the registered flaws.

Hence, the main idea which induced these investigations, the prospective employment of reflected laser radiation for diamond coating patterning, gave several results: a proper evaluation of effects and concluding with possible applications.

CONCLUSIONS

– Irradiation of a mirror-polished substrate surface in a spectro-absorbing diamond precursor atmosphere during hot filament-pulsed CO_2 laser synergy enables obtaining a reflection spot, *i.e.*, a specific coating pattern, to be obtained.

– Laser radiation multiple pass/reflection through a spectro-absorbing precursor atmosphere moderates/eliminates the effects of thermal shock produced by the beam stroke on the surface.

– This procedure of coating patterning is recommended for applications insensitive to nanoscale surface flaws.

Acknowledgements. This work was financially supported by the Ministry of Science and Technological Development of the Republic of Serbia, under projects 142065 and 142067.

ИЗВОД

ЛАСЕРСКИ СПОТ РЕФЛЕКСИЈЕ КАО ШАРА У ДИЈАМАНТСКОЈ ПРЕВЛАЦИ – МИКРОСКОПСКО ПРОУЧАВАЊЕ

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Дијамантске превлаке депоноване су спрегнутим и синхроним деловањем методе усијаног влакна ХДП и импулсног CO_2 ласера у спектроапсорбујућој и спектронеапсорбујућој атмосфери дијамантског прекурсора. Добијене превлаке су структуриране/ишаране, тј. садрже непрекривене, огољене области. Додатни ефекат, запажен само у спектроактивној атмосфери дијамантског прекурсора, јесте формирање још једног ласерског спота у превлаци – рефлексионог спота. Опсежна микроскопска истраживања урађена су имајући у виду морфолошке промене у споту директног ласерског зрака, са циљем да се утврди практична употребљивост рефлексионог спота. СЕМ микрографије нормалне инциденције овог спота показују глатку површину без оштећења импулсним зрачењем. АФМ техника визуализације открила је право стање површине и дала је прецизне податке о њеним карактеристикама.

(Примљено 3. јула 2008, ревидирано 13. марта 2009)

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