Positioning of Carbon nanostructures on metal surfaces using laser acceleration and the Raman analyses of the patterns

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Abstract
The laser-induced acceleration of nanoparticles using intense light irradiation was used for positioning and ordering of carbon nanomaterials to form periodical surface structures. Such systems are of interest for different nanotechnology applications. The nanodiamond with averaged size 100 nm, and fullerene (C$_{60}$) suspended in distilled water were accelerated using high focused laser beam and attached onto metal surface of silver and gold thin films evaporated on Si substrate. The laser was operating both in CW and femtosecond modes with the wavelength of ~800 nm, pulse duration 150 fs, and average laser power of 300-600 mW. In case of pulse irradiation the repetition rate of 76 MHZ was applied. The nanoparticles were positioned on the metal surface in accordance with a predetermined program to allow patterning of the nanoparticles. The positioning was analyzed for different treatment conditions and compared to the calculated data. To investigate the obtained nanoparticles/metal structures, surface-enhanced Raman scattering (SERS) was used utilizing its high sensitivity on the local properties of the nanostructures. SERS allows the observing of carbon nanostructures with their characteristic peculiarities, such as blinking effect and selective enhancement. Here we try to explain the spectral and spatial peculiarities occurring during the laser acceleration process and the interaction of attached carbon nanostructures with metal surface.

1. Introduction
The effect of light pressure on material particles was discovered by Lebedev [1] in the beginning of the last century and was successfully applied during the last 30 years in different investigations including nano- and microparticles, molecular and atom physics, biological and medical researches of light trapping and acceleration of small particles [2]. Practically the same mechanisms are used currently for superfine surface cleaning from micro- and nano-sized contaminations [3], laser-guided direct writing (LGDW) of living cells [4], and laser formation of nanoparticles image inside a microstructure [5]. The feasibility of light-induced acceleration of charged and polarizable particles were first addressed by Askaryan in 1962 [6]. Acceleration by laser was demonstrated for the particles flow inside a cylindrical region in dense random media [6, 7]. Several mechanisms exist for the laser-induced acceleration of microparticles in addition to the light pressure: heating and motion of the medium (convective motion), heating of the surface of an absorbing particle (radiometric motion) and pressure at particle evaporation (reaction pressure). With high absorbing coefficient, all these mechanisms can be much more effective than the light-induced acceleration itself.

Ordering nanomaterials in nanoscale, periodical structures has recently been developed for the purpose of creating new materials and devices [8]. Diamond is considered to be an excellent candidate for the applications owing to its unique physical and chemical properties. The patterning of diamond and diamond-like materials (DLM) is the key process in applying diamond technologies for
microelectronics, and biochip construction, etc. Well-developed method includes chemical vapor deposition (CVD), often in combination with the selective area growth method [9-10]. Methods of deposition of diamond micro- or nanocrystals have also been recently developed [11].

In this study, the nanodiamond with averaged size 100 nm and fullerene (C_{60}) suspended in distilled water were accelerated by high focused near infrared laser beam, and attached onto Ag and Au films surface. The laser acceleration allows the nanoparticles to be positioned and ordered on the surface, forming assigned periodical structure, and to penetrate in metal layer. Upon the nanoparticles/laser beam treatment, the nanodiamond-Ag surface structure was analyzed with scanning electron microscopy (SEM). The analysis was conducted for different laser treatment conditions and compared to the calculated data. The obtained nanoparticles/metal structures analysis was also carried out using surface-enhanced Raman scattering (SERS) technique. This method was found very sensitive to the local properties of carbon nanostructure, such as spatial distribution of different types of hybridization and hence different carbon phases in nano-scale. SERS occurs at target molecules adsorption onto nanometer-sized roughened noble metal surfaces. Nanoscale roughness supports the electromagnetic (plasmon) resonance, which can increase the scattered intensity by 10^4. A second, chemical mechanism is the formation of new electronic states due to adsorbate-substrate bonding interactions. Used dominantly for the study of organic molecules [12], SERS spectroscopy also exhibits high efficiency in revealing the structure and physical properties of nanodiamond films, DLM [13-15], and fullerenes [16-17]. In our experiments strong interaction between the accelerated nanodiamond and Ag was achieved, allowing possible SERS observation [18].

2. Materials and Methods

Synthetic diamond powder with the averaged size 100 nm (Kay Industrial Diamond) and fullerene (C_{60}, Aldrich) were used. After conventional acid washing, the nanodiamond was suspended in distilled water. Water suspension of fullerene or nanodiamonds was stirred or sonicated following sedimentation and separation to remove the largest aggregates. Such suspension contained C_{60} molecular clusters or micro- and nanocrystals with wide size dispersion [19].

Metal films were prepared by deposition of Ag or Au on Si [100] wafers using CVD method with a Thermal Boat Evaporator System (ULVAC). Depending on the evaporation time, thickness of films varied in the range of tens of nanometers as measured with SEM (JEOL JSM6500F). The Si wafer with evaporated metal film was firmly fixed on the microscope stage. A drop of suspension was placed on the film and closed with a cover glass (with the thickness of 0.14 mm). The space between cover glass and substrate was controlled with a gasket (0.15 mm ± 0.02 mm thick).

Particles were accelerated using a femtosecond Ti:sapphire laser (Mira-900, Coherent) with the wavelength of 800 nm, pulse duration 150 fs, average power up to 600 mW, and repetition rate of 76 MHz, pumped by a solid-state laser (Verdi, Coherent). The laser was connected with the modular microscope (IX71, Olympus) and XYZ- scanning programmed stage (SGSP (MS) 20-85, Sigma-Koki). Laser beam was focused with Olympus objectives 4×/0.1, 40×/0.65 and 100×/0.90. After the beam adjustment the scanning of target realized positioning of the accelerated nanodiamond on the target according to the predetermined program. The automatic monitoring and steering was carried out with a stage controller (Mark-204-MS, Sigma-Koki), equipped with a fully closed-loop control system. Two-coordinates scanning with fixed rate was carried out. The treated area for every sample was 2×2 mm². After scanning the cover glass was removed, the sample was carefully washed by distilled water and dried with convection airflow. The obtained samples were investigated using SEM. Raman spectra were measured with AlphaSNOM (Witec) functioning as a confocal micro-Raman spectrometer with Nikon objective 100×/0.90, and 488 nm excitation wavelength (Melles Griot 43 Ion Laser). Spectra were measured with laser beam power at 1-10 mW in focal spot.

3. Results and Discussion

SEM images of the nanodiamonds attached on the Ag surface using femtosecond laser mode, are shown in Figure 1. The ordered surface structure was formed (Figure 1a) with the beam focused
through the 4×/0.1 objective at the average laser power 600 mW. In Figure 1b a few nanodiamond particles of 100 nm can be seen on the surface. The laser-accelerated diamond nanoparticles can penetrate deeply in metal layer and even locally destroyed when using the objectives of 40×/0.65 and 100×/0.90 for laser focusing. In Figure 1c, the penetration/destroyed nanodiamonds using 300 mW power and 40×/0.65 objective is presented. The surface effect is similar to the result of the surfaces cleaning from micro- and nanoparticles with high power light impulse [3], with power high enough to tear the particles away from surface. Van der Waals force is typically predominant adhesion force for particles of less than a few microns in size. Nevertheless the numerical calculation for Van der Waals force at the given experiment conditions have shown that it can be a few orders lower than the force affecting Rayleigh particles stream upon laser irradiation. Moreover, because of high repetition rate of the laser and relatively slow particles’ motion, additional mechanisms to tear particles from surface and even evaporated layer from substrate (see Figure 1c) can be seen, such as laser induced surface vibration, particle vibration, particle thermal expansion and ablation.

The same effect could explain the image of positioned fullerene (Figure 2a): periodically located roundish spots without the particles’ tracks in the center. However, Raman spectra of the fullerene can be observed as shown in Figure 2b.

The obtained nanoparticle-metal structures were analyzed with Raman spectroscopy. Typical Raman spectrum of nanodiamond sample imaged in Figure 1a-b is presented in Figure 3a. Characteristic diamond spectra with peak at 1332 cm⁻¹ were observed. In Figure 3b the spectra of samples obtained in femtosecond regime with objectives 100×/0.90 and power 600 mW are presented.

For samples obtained at high laser power density, the positioning of nanodiamond resulted in deep penetrating into the Ag layer as well as forming nanometer-sized roughness on Ag surface. This is due to the accelerated nanoparticles collisions with Ag. In the same time, the interaction between nanodiamond particles and Ag thin film creates conditions for SERS (Figure 3b, 4). The SERS may be caused both by the strong interaction between the nanodiamond and the Ag film surfaces, and by the influence of electromagnetic enhancement due to the induced nanometer-scaled roughness. In our observation, the separation of these two influences can be difficult. In Figure 4a the Raman spectra for the sample presented in Figure 1c are shown. Complication of the spectra - selective enhancement of some composite bands intensity and repeated increasing and decreasing of Raman signal intensity during sequential measurements (referred as blinking effect), can be clearly observed for the samples subject to laser power about 300 mW using 40×/0.65 and 100×/0.90 objectives (Figure 4).

In Figures 3, 4, the observed Raman bands are: 1332 cm⁻¹ (for carbon sp³ bonding), D-band at 1350 cm⁻¹, and G-band at 1590 cm⁻¹ for carbon sp² bonding graphitic structures, as well as 1150 cm⁻¹ and 1450 cm⁻¹ bands assigned to trans-polyacetylenes [20]. Additional bands relative to the regular bands of carbon structure are observed due to SERS extreme sensitivity to its local nano-scale structural properties. The peak in the range of 1240-1280 cm⁻¹ is characteristic for crystallites in nanometer size [15]. Hydrogenated fragments of hexagonal and tetragonal carbon clusters can give

![Figure 1](image1.png)  
**Figure 1** SEM images of the nanodiamond attached on Ag thin film using 4×/0.1 objective, with laser femtosecond mode with averages power 600 mW. (a) Magnification 430×; (b) magnification 35000×; (c) sample obtained with objective 40×/0.65 and power 300 mW, magnification 50000×.
rise to group of spectral lines around 1300-1350 cm\(^{-1}\) [21]. Splitting of the G-band in 3-4 lines in the range of 1518-1590 cm\(^{-1}\) can arise from the forming of convoluted graphite nanostructures [22]. Due to \(sp^2\)-bonded carbon pairs occupying the position of carbon atom in normal diamond lattice the peaks in the range of 1600-1630 cm\(^{-1}\) can arise, and the peaks in the 1470-1490 cm\(^{-1}\) range demonstrate the existence of vacancies or divacancies with conjugated single and double bonds [23].

Using both Ag and Au as target allowed to obtain samples with similar morphology, but SERS effect exhibited higher sensitivity towards Ag. Some enhancement of characteristic C\(\text{60}\) Raman bands \(A_{2g}\) (near 1470 cm\(^{-1}\), observed with satellite band 1445 cm\(^{-1}\)), \(H_{g7}\) (near 1430 cm\(^{-1}\)), and shifted up to 8-10 cm\(^{-1}\) of \(H_{g8}\) band (1570 cm\(^{-1}\)) were also observed for fullerene on Ag (Figure 2b), and less on Au, that is in agreement with [17].

Comparing CW and femtosecond mode using, at CW mode the laser smelted Ag layer. The forming of ordered nanodiamond surface structures looks impossible, however SERS could still be observed.

Note that the surface structure of the nanodiamond positioned on metal surface by laser acceleration

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**Figure 2** (a) SEM image of the \(C_{60}\) attached on Ag thin film using 100×/0.90 objective. (b) The Raman spectra of image in (a). b(1) the spectrum corresponding to image (a), b(2) the spectrum of \(C_{60}\) on Si. Laser power for Raman detection is 0.5 mW in focal spot.

**Figure 3** The Raman spectra from the samples obtained with average power 600 mW (a) objective 4x/0.1; (b) 100×/0.90. Laser power at Raman detection is 0.5 mW in focal spot. Duration of spectrum measurements was 10 sec.

**Figure 4** The Raman spectra from the samples obtained with average power 300 mW (a) objective 40x/0.65; (b) 100×/0.90. Laser power at Raman detection is 0.5 mW in focal spot. Duration of spectrum measurements was 10 sec.
can be complicated due to the nanodiamond transformation at laser treatment and mechanical collisions with Ag target. The diamond-graphite transformation at high contact compression on diamond was earlier observed by Gogotsi et al. [24]. High temperature due to laser acceleration can also create condition for local structural transformation of diamond nanoparticles, and reflects in the changes of Raman spectra [25]. Structural and shape transformations connected with deformation presumably has been observed for nanodiamond, but not for fullerene – crystal structure can be deformed at used conditions, but not molecular one.

4. Conclusion.
A novel method of nanoparticles ordered positioning via laser acceleration is presented. Morphological (with electron microscopy) and spectroscopic (SERS) analysis of samples provide with the control over positioning conditions and their individual adjustment in accordance with the requirements. This method can be used for surface nanostructures construction, preparation of samples for nanoparticles properties investigation, e.g. diamond-graphite transformation in nanodiamond and features of SERS in nanostructured materials.

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