Blister-based laser-induced forward transfer of 1D and 2D carbon nanomaterials

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Abstract. The possibility of laser printing of single-walled carbon nanotubes (SWCNTs) and graphene via blister-based laser-induced forward transfer technique is demonstrated. Laser radiation with optimized fluence, that is absorbed in a thin aluminium film, causes its local evaporation and blistering without rupture, which leads to the ejection of carbon nanomaterial from the donor to the receiving substrate. The use of preliminary cutting of the donor layer into square pixels allows printing SWCNTs while maintaining their shape. Raman analysis indicates the transfer of carbon nanomaterials without significant degradation.

1. Introduction
The problem of manipulating carbon nanomaterials plays a significant role in the fabrication of new optical elements. Beam lithography, often used for this purpose, requires multi-stage sample preparation and leads to significant contamination of material with polymer and resist residues, which negatively affects its physical properties [1]. Laser-induced forward transfer (LIFT) is a promising technique for the deposition of any material on the desired substrate with a spatial resolution of the focusing laser spot. The principle of the method is the absorption of laser radiation in a thin layer, which generates a strong increase in local pressure, and, as a result, the ejection of transferred material from the donor to acceptor substrates. The review of this method and its application can be found elsewhere [2]. LIFT technique using a polymer as an absorbing layer has already been applied to the fabrication of SWCNTs and graphene patterns [3, 4]. Distinctive features of our approach are, firstly, the usage of metal sublayer to induce blistering for the ejection of the covering donor material, so-called blister-based LIFT (BB-LIFT), and, secondly, the transfer of pure SWCNTs and graphene without polymer films because further removal of the polymer will not be possible without additional damage of the carbon film. The advantage of the usage of a metal film is an isolation of the carbon material from the laser radiation and hot vapor confined inside the blister that excludes the contamination of the received substrate and reduces the heating of the transferred material.

2. Experimental

2.1. Preparation of the donor samples for laser transfer
First, an aluminium film was deposited on the surface of a polished quartz plate in vacuum chamber at a pressure of $10^{-5}$ mbar from a molybdenum boat heated to the temperature of 900 °C by an electric
current passed through it. Then, prepared donor substrates were covered with carbon materials of two types: single-walled carbon nanotubes and graphene. The thicknesses of the aluminium film were 500 and 420 nm for SWCNTs and graphene, respectively. SWCNTs (Sigma-Aldrich, diameters 0.7–1.4 nm) were deposited on the donor surface using an airbrush from a suspension with N-methyl pyrrolidone solvent. The details of this procedure can be found elsewhere [5]. The mean thickness of the resulting layer of SWCNTs was 200 nm. For the second type of donor substrate, the polycrystalline graphene film first was grown on copper foil by chemical vapour deposition and then it was transferred onto the donor by a standard wet method using PMMA as a supporting polymer [6,7].

2.2. Laser transfer technique
We use a top-hat beam of the excimer KrF laser (wavelength 248 nm, pulse duration 20 ns) as the radiation source. The radiation of the laser was focused into a square spot (60x60 μm²) on the surface of the aluminium film. Absorbed laser energy induced the evaporation of a thin metal layer, which led to the blister formation and, as a result, the ejection of carbon nanomaterial occurred. Then the transferred material fell onto the acceptor substrate. The distance between the donor and acceptor substrates was 30 and 50 μm for SWCNTs and graphene transfer, respectively. In our recent work, we used one-stage laser irradiation of the donor to print the pure nanotubes [5]. But the imprint on the acceptor substrates looks inhomogeneous and does not keep the shape of the square laser spot. So we propose to cut the boundary of the transferred area at the first stage of laser irradiation by use of the mask of a special form and laser fluence inducing ablation of the metal film. At the next stage, we used the square mask for the transferring of carbon nanomaterials. The laser fluence ranged from 0.2 to 1.6 J/cm². Pure silicon substrates were chosen as the acceptor for the SWCNTs and with 90 and 290 nm thick layers of silicon dioxide as the acceptor for the graphene film to make possible its visualization on the substrate surface by optical methods.

2.3. Optical and structural analysis
The optical images of the donor and acceptor substrates were analysed by the use of an optical microscope Axiotech 25HD (Carl Zeiss) in reflection and transmission mode. Transmission mode was used to control the metal rupture on the donor substrate after the laser irradiation. The presence of carbon nanomaterials on the donor and acceptor substrates and their possible structural changes after the laser transfer were controlled by Raman spectroscopy. The Raman spectra were recorded in the backscattering geometry using a Horiba LabRAM HR Evolution spectrometer (λ = 532 nm).

3. Results and discussion

3.1. BB-LIFT of SWCNTs
The fluence threshold of the aluminium ablation from the donor sample found in the preliminary experiments is 1.6 ±0.1 J/cm². Therefore the maximum fluence used for transfer SWCNT’s is 1.5 J/cm². The result of the BB-LIFT of the nanotubes is presented in figure 1. The optical images in transmission and reflection modes of the donor substrate after the laser irradiation with different fluence are shown in figures 1 (a) and (b), respectively. The acceptor substrate is presented in figure 1 (c) in a mirror image with the aim to put the corresponding pixels of the donor and acceptor substrates on top of each other. The SWCNTs start to transfer after the irradiation with laser fluence exceeding the value of 0.4±0.1 J/cm², and the pixel on the acceptor substrate looks uniform with a shape corresponding to a square laser spot. With the increase of the laser fluence, the transferred material is divided into fragments of tens of microns in size. The presence of SWCNTs on the substrate has been controlled by Raman spectroscopy (figure 2). For each laser fluence, two spectra were recorded: one on the donor (black lines) and another on the acceptor samples (red line). The Raman spectrum of the SWCNT film on the donor substrate before the laser irradiation is presented by the black line on the top in figure 2. SWCNTs have Raman spectrum where the most intensive modes are the radial breathing modes in the range of 100-400 cm⁻¹ and split G mode at around 1590 cm⁻¹. In the case of
partial or total oxidation/destruction of nanotubes, the intensity of all modes should decrease proportionally to the number of nanotubes present on the substrate. The Raman spectra relating to the donor substrate irradiated with low laser fluence demonstrate lower signal intensity than the original film. This is the evidence of the removal of most SWCNTs from the donor sample, however, part of them remains on the substrate. Increasing the fluence to a maximum value below the threshold allows removing all nanotubes from the donor. The Raman spectra from the acceptor plate indicate the presence of SWCNTs in all cases of laser irradiation. The maximum intensity of the signal is observed for the maximum value of laser fluence. Therefore, it seems reasonable that inertial force caused by the minimum laser fluence is not enough to push the SWCNT film completely from the donor substrate, but it does not induce film rupture, thus permitting to keep the pixel shape.

3.2. BB-LIFT of graphene

The optical images of the donor sample covered by the graphene film and the receiver substrate after the BB-LIFT procedure are shown in figure 3. In the case of graphene transfer, the thickness of the aluminium film on the donor substrate is thinner than for SWCNTs, so the threshold of metal ablation reduces to the value of 0.8 ± 0.1 J/cm². The minimum fluence induced the transfer of graphene also drops (0.20 ± 0.05 instead of 0.4 ± 0.1 J/cm²). Another reason for the threshold reduction is the difference in the thickness of the transferred material, which is a key parameter in heat dissipation in our case of the use of long pulse duration (20 ns) for the BB-LIFT technique. The thickness of the SWCNT film is 200 nm, and the graphene film mainly consists of single layer, as evidenced by Raman spectroscopy (figure 4 – black spectrum). Distinctive graphene peaks were detected at a Raman shift of 1580 cm⁻¹ (peak G) and 2670 cm⁻¹ (peak 2D). The first peak characterizes the sp²-hybridization of carbon and is the main peak in graphene and graphite. The band 2670 cm⁻¹ is responsible for the two-phonon interaction in graphene and allows one to determine the number of its layers. In our case the width of 2D-band is around 32 cm⁻¹, which corresponds to the single graphene layer. The signal to noise ratio is higher for the original film because the spectrum was recorded from the graphene film on the aluminium layer on the donor surface in contrast to the spectra recorded from the silicon acceptor substrate. After the BB-LIFT procedure, the 2D- and G-modes shift to the lower wavenumbers, which indicates the appearance of the stress and bending [8]. Optical images of the acceptor sample demonstrate the presence of micrometer-scale parts of crumpled graphene film chaotically distributed over the area of transfer. At low laser fluence, a small number of parts of the

![Figure 1. Optical images of donor substrate covered by SWCNT film in the transmission (a) and reflection (b) modes, and acceptor substrate (c). Numbers correspond to the laser fluence in J/cm² used for the transfer.](image)

![Figure 2. Raman spectra of nanotubes, registered from initial film and irradiated spots (laser fluence was 0.4, 0.6 and 1.5 J/cm²) on donor substrate (black lines) and from corresponding areas on the acceptor substrate (red lines).](image)
graphene film is observed. An increase in fluence leads to an increase in the number of these parts. No continuous film is observed in any case of irradiation in contrast to SWCNTs. This can be explained by the lower mass of single-layer graphene compared to a 200 nm thick SWCNT film, and generated inertial force is not enough to push graphene film keeping its shape.

Figure 3. Optical images of donor substrate covered by graphene film in the transmission (a) and reflection (b) modes, and acceptor substrate (c). Numbers correspond to the laser fluence in J/cm² used for the transfer.

Figure 4. Raman spectra of graphene films, recorded from the initial film and areas on the acceptor substrate.

4. Conclusions
The BB-LIFT of SWCNTs and graphene is demonstrated. The use of a metal layer absorbing laser radiation and its preliminary cutting into square pixels made it possible to preserve not only individual nanotubes, but also areas of nanotubes comparable with the laser spot size while maintaining the initial structure after the LIFT. This technique used in the case of graphene allowed us to laser print it onto a silicon substrate. However, this approach requires optimization of the transfer conditions of the graphene film fragments while preserving not only structural parameters, but also the shape of the transferred pixel in accordance with the spot of laser radiation.

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