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Penetration of liquid metal droplets through membranes based on single-wall carbon nanotubes

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The probability of penetration of droplets with different sizes (20 nm $\sim$ 1 μm) through a thin ($\sim$ 90 nm) protective membrane based on single-walled carbon nanotubes (SWCNT) has been experimentally determined. It is shown that the probability of penetration of droplets less than 200 nm in size through the SWCNT membrane is 0.4%. The paper presents the results of comparing the droplets deposition rate in terms of „effective" thickness measured in the experiments and calculated via the RZLINE model. The simulation results are in good agreement with the experimental data.

Keywords: SWCNT membranes, droplet penetration, RZLINE code.

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Extreme ultraviolet lithography at the 13.5 nm wavelength is a key technique for producing silicon integrated microchips with the typical size below 8 nm [1]. One of the most topical problems is developing sources of high-frequency electromagnetic radiation for a number of applications: 1) photoresistive layer flare through the projection optics with a photo mask [2]; 2) the photo mask examination for the presence of defects [3]. Operation of the emission sources used in lithography is based on the principles of laser-induced plasma generation. Such sources are characterized by high values of capacity, brightness and energy conversion coefficient. However, there are some difficulties in their employment because of scattering of ions, atoms and droplets contaminating the optical elements [4]. The presence of such contaminations on the surfaces of the lithography machine optical elements reduces the reflectivity of mirrors, which results in power loss on the photoresistive layer. Moreover, the photo mask contamination with microdroplets induces defects in the printed integrated microchips. This is why the development of a protection system for the lithography machine optical elements is extremely demanded. One of the possible solutions is the use of protective membranes to which a number of requirements are imposed, such as high optical transparency and mechanical stability [5]. A promising material for providing protective functions in extreme UV lithography is membranes based on single-walled carbon nanotubes (SWCNT). The SWCNT membranes possess optical transparence $T > 60\%$ in the wavelength range of 1–20 nm ($T = 80\%$ at 13.5 nm) and high strength characteristics [6]. However, the ability of the SWCNT membranes to stop the plasma and microdroplet flows is still poorly studied.

In this work, the probability of penetration of liquid-metal micro— and nano-droplets through the SWCNT membranes is investigated. In the experiment, the droplets were generated due to interaction between the laser pulse and liquid In–Sn target. Analysis of the number and sizes of droplets incident on the SWCNT membrane and passing through it was performed by raster electron microscopy (REM) with subsequent image processing using the ImageJ program code [7], which allowed calculation of probability of the droplet penetration through the membrane.

This work also included verification of the RZLINE-code [8] that simulates such processes causing the droplet release from the target as metal heating with laser radiation, formation of radiating plasma, and formation of pressure shock waves in the liquid phase. For this purpose, calculation of depositing the droplet coating was performed based on the REM images in terms of the „effective" thickness. The „effective" thickness was calculated as a ratio of the total volume of incident droplets to the REM picture area and then compared with the RZLINE calculations.

The experimental facility layout is presented in Fig. 1, *a*. The plasma was generated by a pulsed disk Nd:YVO$_4$ laser produced by EdgeWave ($\lambda = 1.064\,\mu$m, pulse energy 4 mJ, pulse length 1.5 ns, pulse repetition rate 25 kHz). The radiation was focused on the target surface, the focal spot size was 60 μm (by the $1/e^{-2}$ level). As the target, liquid metal placed in the rapidly rotating ($F = 240$ Hz) crucible was used. This approach provided a reproducible plane target for all the laser pulses. The target material was eutectic alloy of In and Sn ($m_{\mathrm{In}}/m_{\mathrm{Sn}} = 48\%/52\%$). A freely suspended SWCNT membrane with typical thickness $d = 90$ nm was mounted at the distance $l = 0.4$ m from the plasma at angle $\theta = 60^\circ$ to the target surface normal. As the SWCNT membranes, commercially available Canatu

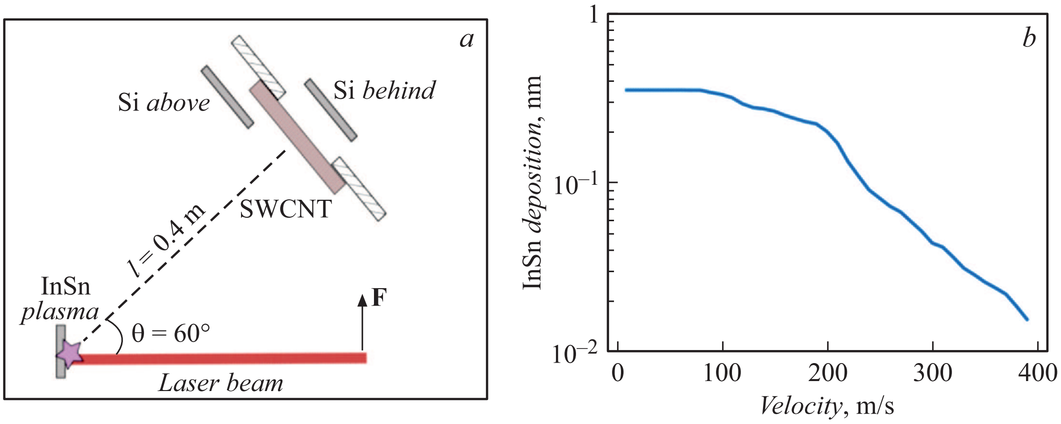

Figure 1. *a* — schematic layout of the experimental facility; *b* — RZLINE simulation of the integrated thickness of the droplet coating on silicon that was formed with the rate exceeding the preset one during $1.71 \cdot 10^9$ laser pulses.

specimens were used. To prevent deposition of plasma ions and atoms on the SWCNT membranes, magnetic field and buffer gas (Ar) at the pressure of 1.5 Pa were used. To characterize the droplets incident on the membrane and passing through it, silicon control samples were set before and behind the SWCNT membrane. After exposing the samples to droplets during $1.71 \cdot 10^9$ laser pulses (19 h of uninterruptible operation of the 25 kHz laser), the Si surface was examined by REM at different amplifications (10k, 1k, 100). To make the sampling more representative, photos of ten different areas of the sample surfaces were made with each amplification factor. Based on the REM pictures, the size and number of droplets on the Si samples were analyzed using the image processing code ImageJ. Droplets with diameters of 20–200, 200–2000 and > 2000 nm were fixed for the 10k, 1k, 100 amplifications, respectively. The ratio between the numbers of droplets found on equal areas of REM pictures of silicon samples placed before and behind the protective SWCNT membrane was just the parameter defining the droplet penetration probability.

Fig. 2, *a* and *b*, demonstrates the case REM pictures of the non-protected silicon sample and SWCNT membrane, respectively, after exposure to droplets during $1.71 \cdot 10^9$ laser pulses. Light areas in the pictures correspond to the In–Sn droplets. Fig. 2, *c* presents the droplet size distribution. Fig. 2, *c* shows that the number of droplets incident on the unprotected with an SWCNT membrane Si sample $1\,\mu\text{m}^2$ in area decreases with increasing droplet diameter.

The numbers of different-size droplets found on the Si sample surfaces are listed in the Table. The Table demonstrates that the penetration probabilities of large (over 2000 nm), medium (200–2000 nm) and small (20–200 nm) droplets are 67, 17 and 0.4%, respectively. Thus, the probability of droplet penetration through the SWCNT membrane 90 nm thick decreases with decreasing droplet size. This may be explained by that the decrease in droplet size and, hence, in its weight, results in reduction of the kinetic energy. There are three versions of the droplet–SWCNT membrane interaction depending on the incident droplet energy: 1) passing through the membrane; 2) change of the droplet motion direction by 180°; 3) inelastic collision with total loss of the motion speed. The first version is most probable for large-size droplets with high kinetic energy, while the second and third versions are most probable for the medium and small droplets.

Notice that the distribution of the small-size incident droplets was uniform, while that after passing through the SWCNT membrane was nonuniform: when large areas of the samples were scanned, only a few REM pictures exhibited units of droplets. This allowed us to conclude that droplets pass through the SWCNT-membrane without fragmentation.

Assuming that each droplet in the REM photo is a sphere, it is possible to calculate the uniform „effective“ thickness of the droplet coating formed during the experiment. The calculated „effective“ thicknesses of the coating formed by small—, medium— and large-size droplets on the Si sample placed before the protective membrane are 0.001, 0.061 and 0.262 nm, respectively. Thus, the total „effective“ thickness of the droplet coating is 0.32 nm.

To describe theoretically the deposition rate, the RZLINE code was used. Fig. 1, *b* presents the calculated „effective“ thickness of the coating deposited during the experiment ($1.71 \cdot 10^9$ laser pulses) from the liquid Sn + In phase (in droplets) with the rates above the preset one; the coating was deposited at the distance of 0.4 m from the source. The figure shows that the main contribution to the droplet deposition comes from the particles with speeds below 200 m/s, while the maximum droplet speed does not exceed 400 m/s. The total coating thickness is about 0.34 nm. Notice that the RZLINE code does not take into account the surface tension forces, which makes impossible calculation of the droplet distribution by their diameters, and, hence, only the „effective“ coating thickness undergoes

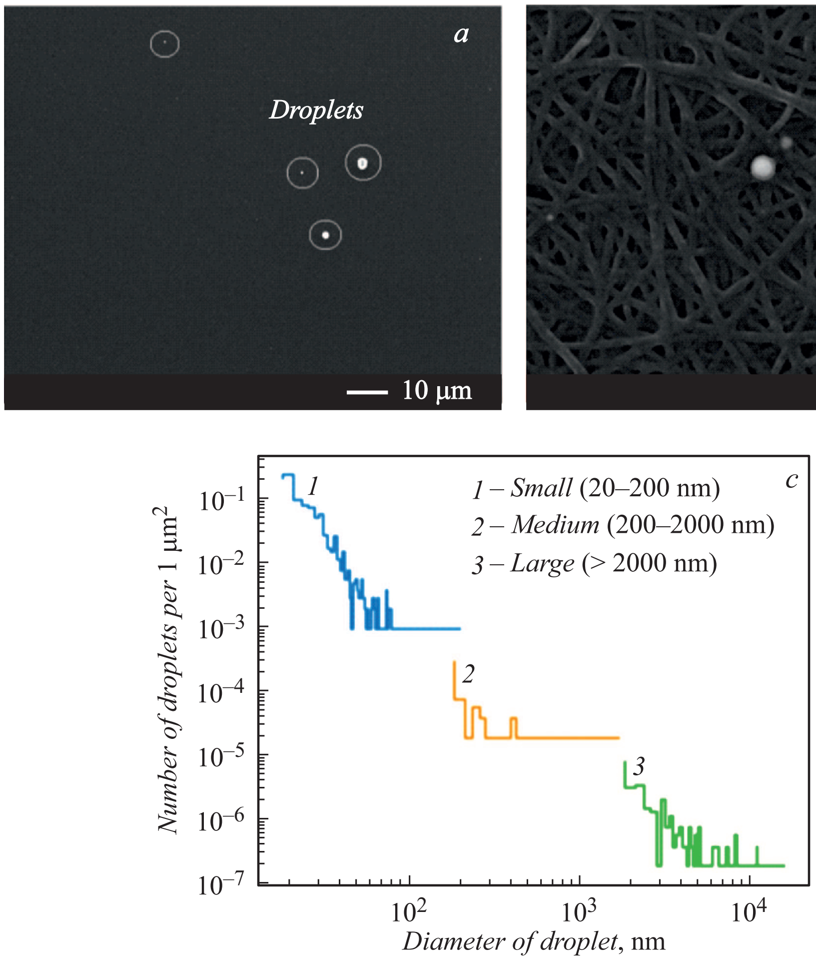

Figure 2. *a* — REM photo of the silicon sample exposed to droplets; *b* — REM photo of the SWCNT membrane; *c* — histogram of the particle size distribution.

Distribution of the average number of plasma droplets on the Si samples placed before and behind the protective SWCNT membrane (in brackets, the REM photo area is indicated)

Sample position	Small droplets 20–200 nm (10^{-3} mm^2)	Medium droplets 200–2000 nm (0.053 mm^2)	Large droplets > 2000 nm (5.3 mm^2)
Before SWCNT	1078	35	168
Behind SWCNT	4	6	112

the comparison. The coating thickness calculations are in good agreement with experimental data; due to this it becomes possible to verify the target sputtering model comprised in the RZLINE-code.

The obtained results demonstrate that thin (90 nm) SWCNT membranes efficiently suppress the droplets 20–200 nm in size thus providing the penetration probability of 0.4%. The droplet penetration probability is shown to increase with increasing droplet size. The paper presents the RZLINE calculations of the coating deposition rate in terms of the „effective" thickness, which are in good agreement with the experimental data.

Conflict of interests

The authors declare that they have no conflict of interests.

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