Renewable single-walled carbon nanotube membranes for extreme ultraviolet pellicle applications

Javier A. Ramirez B., Dmitry V. Krasnikov a,++ , Vladimir V. Gubarev b, c, Ilya V. Novikov a, d, Vladislav A. Kondrashov a, Andrei V. Starkov b, Mikhail S. Krivokorytov c, Vyacheslav V. Medvedev b, c, Yuriy G. Gladush a, Albert G. Nasibulin a, d, *

a Skolkovo Institute of Science and Technology, Nobel 3, 121205, Moscow, Russia
b Moscow Institute of Physics and Technology (State University), Dolgoprudny, Moscow Region, 141701, Russia
c Institute for Spectroscopy of the Russian Academy of Science, Moscow, Troitsk, Russia
d Aalto University School of Chemical Engineering, Kemistintie 1, 02015, Espoo, Finland

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ABSTRACT

We propose a facile, cost-efficient, environmentally friendly, and scalable process to renew single-walled carbon nanotube membranes serving as extreme ultraviolet (EUV) protective pellicles. The method comprises of high-temperature treatment of the membrane by Joule (resistive) heating at temperatures higher than 1000 °C and pressure below 0.3 Pa. Using model Sn aerosol nanoparticles, the primary contaminant from extreme ultraviolet light sources, we demonstrate the proposed method to clean the membrane with the power consumption as low as 20 W/cm². We show the proposed method to cause no harm to carbon nanotube structure, opening a route towards multiple membrane renovation. We confirm the applicability of the approach using in situ deposition from the semi-industrial EUV light source and subsequent Sn-based contaminant removal, which restores the EUV-UV-vis-NIR transmittance of the film and, therefore, the light source performance. The proposed method supports pulse-cycling opening an avenue for enhanced protection of the lithography mask and stable performance of the EUV light source. Additionally, the approach suits other composite contaminants based on such species as Pb, In, Sb, etc.

1. Introduction

Semiconductor-based integrated circuits defined the development of humankind during the last 60 years. Throughout the several game-changing innovations that ensured the field to be concealed in the empirical Moore’s law [1], the transistor industry inevitably pursues the limits of the engineering of the matter [2]. Extreme ultraviolet (EUV) lithography is considered the next large step to continue the silicon life cycle in the nearest future. The method employs 13 nm ultraviolet light to achieve features down to 5 nm [3]. One of the key challenges for the technology is to protect the EUV mask from particles emitted by the light source [4], which converts far infrared radiation from a CO₂ laser into broadband EUV by triggering plasma over micrometer-sized Sn droplets [5,6]. The subsequent quenching of the plasma generates aerosol nanoparticles inside the EUV projection machine that can contaminate the mask and, thereby, harm the lithography process.

Among various methods to protect the EUV mask from aerosol contaminants [7–12], shielding with a pellicle is considered to be one of the most efficient. The EUV pellicle is a membrane with low absorption around 13 nm, high mechanical and chemical stability [13,14]. Graphene [15], silicon and silicon nitride [16], multi- and single-walled carbon nanotube [17], thin carbon films [18], graphite [19], and alternative solutions [20] have been already employed as protective membranes with different efficiency. Naturally, the protection by the pellicle decreases with the time due to the contamination by tin-based particles emitted by the EUV source [3,21]. Owing to the high natural EUV absorption of all the materials, removal of the deposited Sn particles from the pellicle might be a key for significant enhancement of the both EUV source performance and EUV lithography in general. Various ex situ methods comprising etching with H₂ or He plasma, laser-induced
shockwave cleaning, carbon dioxide snow cleaning, wet cleaning, ultrasonic/cavitation cleaning have been examined to remove the deposited Sn particles [22–27]. Nevertheless, besides other limitations, the utilized methods require the extraction of the membrane from a vacuum chamber or extra units inside a lithograph that can damage the pellicle, mirrors, or machine.

In the present work, we propose an original and elegant solution for repetitive membrane renovation employing Joule heating to remove contaminant particles from the surface of the SWCNT nanotube membrane. We develop our approach using advances of Joule-heating induced evaporation of the catalyst residuals to improve the performance of high-quality carbon nanotubes in thermophones and bolometers [28]. Here, we employ multiple treatment with excessive amount of external contaminants for protective membrane based on SWCNT with moderate defectiveness. To remove any possible effect of EUV-induced damaged or plasma, we employ a model aerosol of Sn particles with controlled size distribution produced by a spark discharge generator [29]. Using a set of methods, we track the Sn contaminant evolution on the surface of the SWCNT pellicle prototype (electron microscopy combined with element analysis) and changes in the SWCNT structure (Raman and UV–vis–NIR spectroscopies). Moreover, to ensure the viability of the proposed approach, we integrate and examine the renewable free-standing SWCNT pellicle in the EUV radiation source chamber.

2. Experimental section

Single-walled carbon nanotube (SWCNT) membranes were produced by an aerosol (specific case of a floating catalyst) chemical vapor deposition (CVD) method discussed in detail elsewhere [30]. In brief, Fe-based catalyst precursor (ferrocene, Sigma Aldrich, 98%) was injected in a tubular quartz reactor at 400 °C in the CO/CO2 atmosphere (99.99% CO, 99.995% CO2). The Boudouard reaction \(2 \text{CO} \leftrightarrow \text{C} + \text{CO}_2\) takes place at 880 °C on the surface of iron particles to produce nanotubes with an average diameter of c.a. 1.2 nm. The SWCNT films were collected at the outlet of the reactor by simple filtration from the gas phase on the surface of a nitrocellulose filter (HAWP, Merck Millipore, USA) as a randomly oriented network. To obtain a free-standing membrane, SWCNT film was then transferred on the electrodes (304L stainless steel tube with a diameter of 0.8 mm) by the dry transfer technique [31]. To remove the Fe catalyst, the purification of the free-standing SWCNT membranes was done with Joule (resistive) heating for 3 min at 1400 °C according to the procedure described previously [28] and these purified samples are denoted as “pristine pellicles”.

To produce model aerosol Sn nanoparticles, we utilized a spark discharge generator discussed in detail elsewhere [32]. A high voltage power supply, Heinzinger PNC 20000-10 ump (Germany), provides energy to trigger an arc discharge between cylindrical shape Sn electrodes (99.926%; InTechSplav, Russia), leading to plasma formation followed by fractional evaporation of the electrode material. These electrodes are subjected to the flow of N2 carrier gas (99.999%), being controlled by a mass flow controller (Alicat MC series, USA). The flow containing the Sn aerosol passed through the SWCNT film as shown in Fig. 1A. The number size distributions of the Sn aerosol were studied using a differential mobility analyzer combined with a nanoparticle enhancer and a condensation particle counter (DMA-CPC, TSI corporation, USA, 3938 series, 3977 Nano Enhancer, 3977 CPC) capable of measuring the particles with an effective diameter from 0.7 up to 60 nm.

It is worth mentioning that the data processing was carried out with
standard software of Scanning Mobility Particle Sizer Spectrometer, i.e., assuming the spherical shape of the aerosol particles. It is worth noting that an equilibrium vapor pressure of Sn [33] is comparable to or exceeds the chamber pressure at T > 800 °C (Fig. 1B). According to literature data describing Fe–C–Sn [34] and Al–C–Sn systems [35], the carbon solubility in Sn is less than 2 × 10⁻⁶% at T < 1500 °C [33], which allows us to assume carbon and tin to have no chemical reactions in the range studied.

The purification of the film from Sn particles was carried by Joule heating out in the vacuum chamber (P < 0.3 Pa), using Pfeiffer hi-cube 80 vacuum station (Germany) with a vacuum gauge (Pfeiffer MPT100, Germany) discussed in detail previously (Fig. S1) [28]. The sample was heated in a single step (Fig. 1C and D) by direct current (DC) with a power source Electro Automatics 3200-04C (Germany). The temperature of the film was controlled with a pyrometer (Euromix RXR 2300, Russia) in the range from 600 to 2300 °C on the basis of spectral response from 1.0 to 1.6 μm (Fig. 1E). A detailed description of the calibration procedure for the pyrometer is described elsewhere [28].

Optical spectroscopy measurements were performed using Perkin Elmer Lambda 1050 UV–vis–NIR spectrometer in the range of 200–3200 nm with a resolution of 1 nm. Thermoscientific DXRxi Raman Imaging microscope with a laser excitation wavelength of 532 nm was used for Raman spectroscopy measurements. Raman spectra were normalized to G mode intensity. The free-standing membranes were transferred on a TEM lacey Cu-300 grid and observed with a FEI Tecnai G2 F30 transmission electron microscope. For SEM examination, free-standing samples were placed with their holders on aluminum support with carbon tape, observed, and mapped using FEI Teneo scanning electron microscope with dual Bruker X-flash EDS detectors.

EUV transmittance measurements of a free-standing SWCNT membrane were carried out in a chamber of the TEUS-S-100 light source [36], which employs pulsed laser radiation at the wavelength of 1.064 μm with the following parameters: an average output power of 100 W, energy of each pulse of 4 mJ, pulse repetition rate of 25 kHz, and pulse width of 1.5 ns (Nd: YVO₄ laser system from EdgeWave [37]).

3. Results and discussion

3.1. Model Sn aerosol particles

In order to remove any side effects of EUV-induced damage of carbon nanotubes, we employed model Sn aerosol to simulate the deposition of Sn particles on the SWCNT membrane. Sn aerosol particles were chosen as the most of EUV sources employ tin. Fig. 2 depicts particle size distributions of Sn aerosol produced by the spark-discharge generator. All the aerosols show typical lognormal distribution [38] (Fig. 2A) with the geometric mean diameter varied in the range of 2–16 nm, depending on the breakdown voltage, which in turn is a function of the distance between electrodes [39], which was varied in our experiments from 0.01 to 0.5 mm. We employed a breakdown voltage of 0.37 kV to produce the model Sn aerosols at the highest productivity (Fig. 2B). As the employed generator produces 1.5 μg/min of tin [40], estimated by numerically solving the Jones model [41] (Section S1; Table S1), the deposition time was fixed at 4 h to simulate heavy contamination of a pellicle with an areal density of c.a. 6 μg/cm² [42].

3.2. Sn removal

According to TEM (Fig. 3) and SEM (Fig. 4) studies, tin uniformly covers SWCNTs forming agglomerates in the range from several nm to a few μm, reaching the conditions of EUV pellicles. Such a uniform distribution of tin might be also beneficial for Sn/SWCNT composites serving as anodes for Li-ion batteries [43,44].

The vapor pressure of tin [33,42] exceeds the pressure of the chamber at T ≥ 800 °C (Fig. 1B). According to SEM and TEM results, heating up to 1000 °C under 0.3 Pa removes most of the nanoparticles from the nanotube surface leaving only the largest Sn of several microns in size (Fig. 3c; Fig. 4c) while the annealing at the temperature of 1400 °C provides complete Sn evaporation (Fig. 3d; Fig. 4d). It should be mentioned that due to the high thermal conductivity and low thermal capacity of the free-standing film, only nanotubes reach the discussed temperature, while the holder and nearby chamber are relatively cold [28]. The average amount of power to process a 40 nm thick membrane at 1400 °C was about 20 W/cm²; the proportional integrative-derivative power-based output control method of the power supply sufficed to maintain a stable process temperature of around 0.1% fluctuation at 1400 °C.

3.3. SWCNT structure

It is worth noting that most of the recently proposed methods to purify pellicles inevitably result in their partial damage [11,12,22,24,25,27,45,46], while our technique was shown to keep the original structure of the SWCNT membranes (Fig. 3d; Fig. 4d). UV–vis–NIR and Raman spectra of the regenerated membranes also confirm that the structure of SWCNTs practically did not change. Fig. 5 shows an increase in the absorbance after deposition of the Sn aerosol nanoparticles on the surface of the SWCNTs (see also Fig. S2). However, after 5 and 10 cycles of Sn deposition and renovation using Joule heating at 1400 °C for 3 min the UV–vis–NIR spectra remain almost unchanged. Therefore, since no shift or peak decrement is observed the renovation effect on the pellicle properties is negligible [47], opening a way for the approach of multiple renovations. It should be also noted that the maintained spectrum denies significant film densification as no increase in reflectance was observed.

We also observe only minor changes in SWCNT structure with Raman spectroscopy (Fig. 6). The ratio of intensities of G and D modes – a key

![Fig. 2. A) DMA particle size distributions of Sn aerosol produced by the spark discharge generator at different breakdown voltages. B) total concentration and geometric mean diameter of aerosol particles produced at different breakdown voltages. (A colour version of this figure can be viewed online.)](image-url)
Fig. 3. Typical TEM images of SWCNT pellicles: A – pristine pellicle; B – pellicle with Sn deposited for 4 h and then regenerated at 750 °C during 5 s; C – Pellicle with deposited Sn particles and regenerated during 30 s at 1000 °C; D – Pellicle with deposited Sn particles and regenerated during 3 min at 1400 °C. (A colour version of this figure can be viewed online.)

Fig. 4. SEM EDS maps of SWCNT membranes: A – Pristine pellicle; B – Pellicle with deposited Sn particles deposited for 4 h and regenerated during 5 s at 750 °C; C – Pellicle with deposited Sn particles and regenerated during 1 min at 1000 °C; D – Pellicle with deposited Sn particles and regenerated during 3 min at 1400 °C. (A colour version of this figure can be viewed online.)
modes are denoted. (blue); radial breathing modes (RBM; enlarged in the inset) as well as D, G, and 2D starts at temperatures higher than 2000 °C. Defect healing in carbon nanotubes indicator of carbon nanotube defectiveness. Defect healing in carbon nanotubes during 24 h and renovation (during 3 min at 1400 °C). Optical transitions between van Hove singularities for semiconducting (S11, S22) and metallic SWCNTs (M11) are denoted to show that the process preserves SWCNT band structure as well as provides no doping. (A colour version of this figure can be viewed online.)

![Fig. 5. UV–vis–NIR spectra of pristine SWCNT pellicles (black), with tin deposited during 24 h and renovation (during 3 min at 1400 °C). Optical transitions between van Hove singularities for semiconducting (S11, S22) and metallic SWCNTs (M11) are denoted to show that the process preserves SWCNT band structure as well as provides no doping. (A colour version of this figure can be viewed online.)](image)

indicator of carbon nanotube defectiveness – increases implying the etching of defective carbon species during the renovation process and indirectly proving the possibility of multiple renovation cycles. The apparent increase in Ih/I0 ratio is more interesting as implies slight decrease of nanotube defectiveness. Defect healing in carbon nanotubes starts at temperatures higher than 2000 °C [46] which significantly above the range used. We can only speculate that the observed increase in quality might be attributed to a local reconstruction in the vicinity of the Schottky barriers. As the points of the highest resistance, Schottky barriers might empower the higher temperature of the junctions, while the high heat conductivity of carbon nanotubes ensures localization of high temperature zone and limits its direct observation.

Thus, the full recovery of absorption spectrum after renovation together with increase of Ih/I0 ratio demonstrates that SWCNT film successfully survives the heating temperature without loss of the materials or decrease in its quality. It should be also mentioned that the proposed approach is not limited to SWCNT films only (i.e., it can be extended to, for example, nanotube fibers or aerogels [49–51]) or to Sn contaminants - other metals or alloys such as Pb, Co, In, Sb, etc. can be eliminated as well [33].

3.4. In situ renewal

The renewal abilities of the SWCNT pellicles were assessed within the industrial TEUS-S-100 EUV light source [36]. The laser beam was focused on the liquid target (In/Sn alloy with the mass proportion of 48/52) surface with a focal spot size of 60 μm (1/e2 intensity level). The SWCNT pellicle was placed inside the vacuum chamber with the pressure of residual gasses ≤100 mPa at a 40 cm distance from the plasma source. In/Sn aerosol particles were deposited onto the surface of the SWCNT pellicle during EUV source operation. It should be noted that In shows vapor pressure c.a. two orders of magnitude higher than that for Sn (Fig. S3), so the obtained results and regimes optimized can be easily translated to In/Sn composites.

The interaction of the laser beam with the liquid target creates plasma, which apart from generation of EUV radiation emits In/Sn species (atoms, ions, and mostly aerosol particles) onto the surface of the SWCNT pellicle (Fig. 7 A). Two identical AXUV-100 photodiodes covered with the same spectral purity multi-layered Zr/Si filters (with a period of 4.2 nm, the fraction of Zr layers: 0.67, the number of layers: N = 55) were utilized to measure the power of EUV radiation in the range of 12.5–18.0 nm with a maximum at 13.5 nm (Fig. 7 B). One photodiode measured the incident EUV intensity directly from the plasma, while the other assessed EUV intensity transmitted through the SWCNT pellicle. The ratio of the abovementioned signals determined the EUV transmittance coefficient. Photodiodes were protected by shutters to prevent their degradation during the In/Sn deposition and were opened only for the EUV transmittance measurements.

![Fig. 6. Raman spectra of SWCNT-based membranes (pellicles): pristine (black), after Sn deposition (red) and after renovation at 1400 °C, 3 × 10^{-4} Pa for 3 min (blue); radial breathing modes (RBM; enlarged in the inset) as well as D, G, and 2D modes are denoted. (A colour version of this figure can be viewed online.)](image)

Fig. 8 shows the dynamic of integral (12.5–18.0 nm) EUV transmittance of a free-standing SWCNT membrane measured with a laser-produced plasma In/Sn source. During the first 10 min, the annealing was performed with a DC input power of 10 W/cm2 (c.a. 1150 °C), it was applied while the EUV transmittance was constant ∼0.74. Then, In/Sn deposition (Fig. 8; blue curve) was started and the transmittance of the EUV membrane dramatically dropped from 0.74 to 0.48. After that moment, the deposition with In/Sn species was stopped and DC power was supplied with 1 W/cm2 power (red curve; ∼600 °C) that had negligible effect on the EUV transmittance of the SWCNT membrane. With an increase of input power up to 5 W/cm2 (red curve; ∼900 °C), the transmittance coefficient increased from 0.50 to 0.58. Increasing the input power to 10 W/cm2 (magenta curve; ∼1100 °C) continued In/Sn evaporation without gradient changing. Finally, the EUV transmittance returned to its initial value of 0.74 confirming the applicability of the method with industrial EUV source. Thus, the obtained results verify our method to renew the free-standing SWCNT membranes with a threshold effect on the input power of 5–10 W/cm2. Moreover, the results of the considered manuscript not only unambiguously prove the multiple cycling but also open the route to check other corresponding effects (e.g. degradation of SWCNT membrane under EUV radiation or the role of plasma treatment).

4. Conclusions

We developed a technique to renew EUV pellicles based on SWCNT membranes by means of Joule heating. Using the model tin aerosol and EUV light source deposits, we showed the complete removal of both Sn contamination produced by model aerosol particles and later Sn/in deposited in the EUV light source chamber. We show the Sn-based contaminations to be mostly removed during annealing at 1000 °C for 1 min, while the treatment for 3 min at 1400 °C resulted in complete Sn absence on the pellicle surface. We proved the technology to be energetically efficient as only 20 W/cm2 is needed for the complete
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2022.07.014.

References


Fig. 7. A - Illustration of the experimental setup for the EUV transmission measurement of a free-standing SWCNT pellicle in situ during In/Sn deposition and renovation; B – EUV spectrum of the light source used for the measurements. (A colour version of this figure can be viewed online.)

Fig. 8. In situ evolution of EUV transmission of a free-standing SWCNT pellicle during In/Sn deposition and renovation. (A colour version of this figure can be viewed online.)

renewal of the SWCNT-based pellicle. Moreover, unlike most of the methods for pellicle cleaning proposed so far, the renovation with Joule heating can be performed in situ directly within a EUV lithograph. It should be stressed that the approach did not harm carbon nanotube pellicle as the SWCNTs preserved their morphology, quality, electronic structure, therefore, paving the way for multiple renovation cycles or pulsed processes. Additionally, the approach suits other contaminants (or their composites) in a form of atoms, clusters, or nanoparticles like Pb, In, Sb, etc. This demonstration opened a route towards the design of SWCNT film-based devices to effectively shield the collector and mask from EUV lithographs against the well-known harmful effects of tin and/ or indium aerosol deposition in the walls of the lithograph device and their optical surfaces.

CRediT authorship contribution statement
