Carbon nanotube membranes for EUV photolithography – a versatile material platform

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ABSTRACT

Next generation of high-NA extreme ultraviolet (EUV) photolithography introduces higher power levels and faster reticle accelerations, enabling breakthrough in scanner efficiency. This results in higher temperatures and mechanical stresses on the EUV pellicles. Here we demonstrate scalable carbon nanotube (CNT) membrane mass production from a floating catalyst chemical vapor deposition (FC-CVD) reactor, using a direct dry deposition method. This direct high volume fabrication method yields highly uniform CNT networks with high strength and purity, enabling exceedingly thin CNT pellicles with high transparency at EUV. This end-to-end manufacturing process, starting from reagent gases, enables control and reproducibility over the final nanomaterial product. Control over synthesis allows tailoring of the carbon nanotube diameter and wall count (SWCNT or FWCNT), as well as control over the CNT network morphology such as the density, bundle size, and orientation of CNTs. The combination of this direct fabrication method with the exceptional mechanical and thermal properties of CNTs creates a versatile membrane platform, which can be further modified with post process steps such as purification to remove metal impurities. To enable conformal and thin coatings on CNTs, wet and dry functionalization steps are demonstrated to match the surface chemistry of CNTs to the specific deposition chemistry used in atomic layer (ALD), chemical vapor (CVD), or physical vapor (PVD) deposition processes. Thicker and denser CNT membranes with appropriate coatings are also suitable for other roles, such as filtering debris from an EUV source, blocking DUV photons and electrons, and providing a gas seal for differential pressure.

Keywords: Carbon nanotube manufacturing, dry deposition, CNT membrane, EUV pellicle, debris filter, single walled carbon nanotubes, multi walled carbon nanotubes, few walled carbon nanotubes

1. INTRODUCTION

Extreme Ultraviolet (EUV) lithography is a giant leap forward, yet defects in printing remain among the greatest constraints to EUV technology uptake. One of the breakthroughs that enabled lithography in high-volume microchip manufacturing is the pellicle. Another breakthrough is the increasing source power. The present day EUV pellicle is reaching its physical limits, calling for new material innovations that can cope with these extreme environments. Canatu has scaled up its unique carbon nanotube (CNT) synthesis and free-standing membrane fabrication technologies. These ultrathin CNT membranes can have an EUV transmittance of up to 98 EUV%T, however denser and thicker CNT membranes might be required to ensure particle filtration. They protect the photomask from particles and defects, and can handle high temperatures far exceeding 1000°C. They can be pumped down and vented at high speeds. Overall, CNT membranes are one of the most promising candidates for the next generation EUV pellicle.

When synthesized using Canatu's Floating Catalyst Chemical Vapor Deposition (FC-CVD) reactors, CNTs can be over 10 µm long, but only nanometers in diameter, and can be customized with, for example, different numbers of side walls: single-walled (SWCNT), double-walled (DWCNT) or few-walled (FWCNT), or a desired mix of them. Canatu has developed a special dry process for depositing the FC-CVD synthesized CNTs directly onto any desired substrate or frame. This special direct dry deposition process eliminates any compromising steps, such as wet dispersion steps, resulting in longer, cleaner, and virtually defect-free CNT membranes. These membranes are highly uniform and durable with alternatively stiff or elastic properties. When combined with optimized morphology and additional surface treatments, the exceptional mechanical, optical, and thermal properties of CNTs make them an attractive material for the extreme environments of EUV semiconductor manufacturing.

Compared to conventional thin film pellicles, these ultra-thin freestanding carbon nanotube network membranes can satisfy transmittance requirements with a minimal number of atoms due to the outstanding strength of carbon nanotubes: CNTs form a random network web-like freestanding membrane, which allows the combination of the extreme 1-dimensional tensile strength of a CNT, with the elastic flexibility and versatility of a 2-dimensional network. As exhibited in Figure 1 (B), a typical CNT pellicle of 96 EUV%T forms a rigid network that allows for capturing of nanoparticles, saving the reticle from contamination. A network composed of CNTs several micrometers long can withstand the harsh mechanical and thermal requirements of next-generation EUV lithography.

With Canatu's end-to-end fabrication capabilities, these CNT membranes are not limited to pellicles alone, but they can be used in any environment where there is a need to filter particles, or certain optical properties such as wavelength or electron filtering. It is also possible to tailor the properties of these membranes to more specific requirements by the application of different coatings, enabling further applications, such as debris filtering from certain EUV sources.

2. CNT MEMBRANE FABRICATION

One of the core technologies in CNT membrane fabrication is the unique dry deposition method. As illustrated in Figure 1 (A), CNTs are first synthesized from gases in an FC-CVD reactor, from where these floating CNTs are then collected onto a filter and directly deposited onto an open frame or border, forming the free-standing CNT membrane. These membranes are then post-processed, as per application requirements for example for EUV pellicles, debris filters, or other X-ray filters.

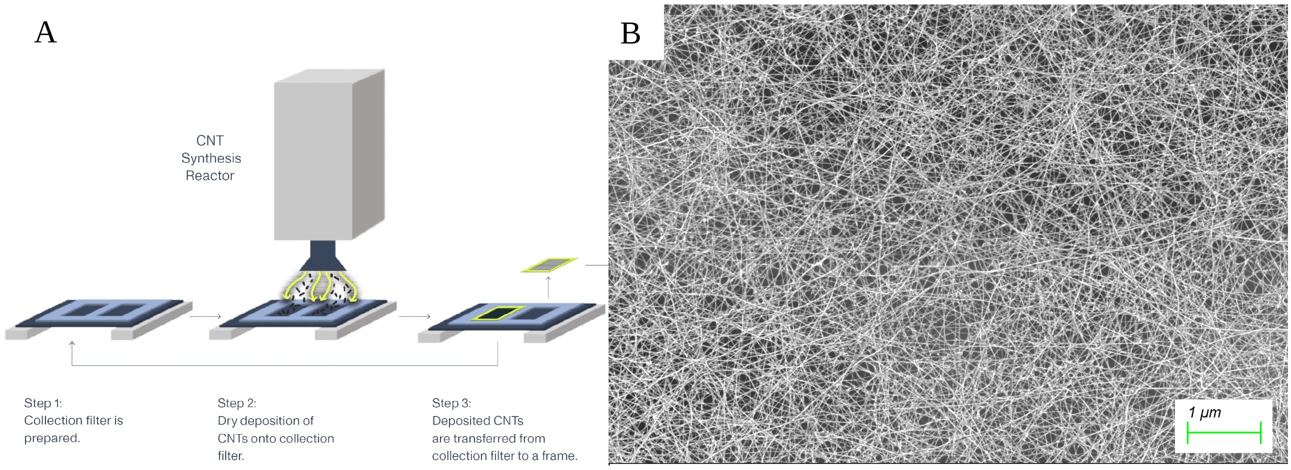

Figure 1. A) Depiction of the FC-CVD synthesis of CNTs and the subsequent direct deposition onto any substrate, frame, or border. B) Scanning electron microscopy image of a 96 EUV%T freestanding CNT membrane prepared in step (A). Note the long and continuous CNTs and bundles.

This simple end-to-end process of CNT synthesis and direct fabrication of CNT membrane also allows for substantial control over the overall properties of the membrane. As illustrated in Figure 1 (B) by scanning and transmission electron microscopies (SEM & TEM), control over the FC-CVD reactor enables the adjustment of both the individual CNT properties, as well as the resulting membrane morphology. One example is the adjustment of the wall count in the carbon nanotubes, as showcased in Figure 2: Having several walls can be for example beneficial in optimizing any covalent coating processes. Tube diameter and chirality can also be adjusted independent of the wall count. The bundle size of CNTs and the overall morphology forming the CNT membrane can be tuned in synthesis to optimize coating processes: For example, limiting the total surface area that requires a coating, or limiting exposure to harmful environments. To further optimize coating properties, the surface chemistry of CNTs can be pretreated in post-processes with targeted surface functionalization. If anisotropic properties are desired – for example mechanical or electrical properties – the orientation of the CNT network can be controlled. In EUV applications, however, isotropic orientation is preferred to minimize any scattering or flare.

Essentially, the FC-CVD synthesis allows control over every element of the process: By controlling the catalyst formation and activation, temperature gradients, reagent gases, and reactor structure, we can create longer tubes with higher functionality and purity.

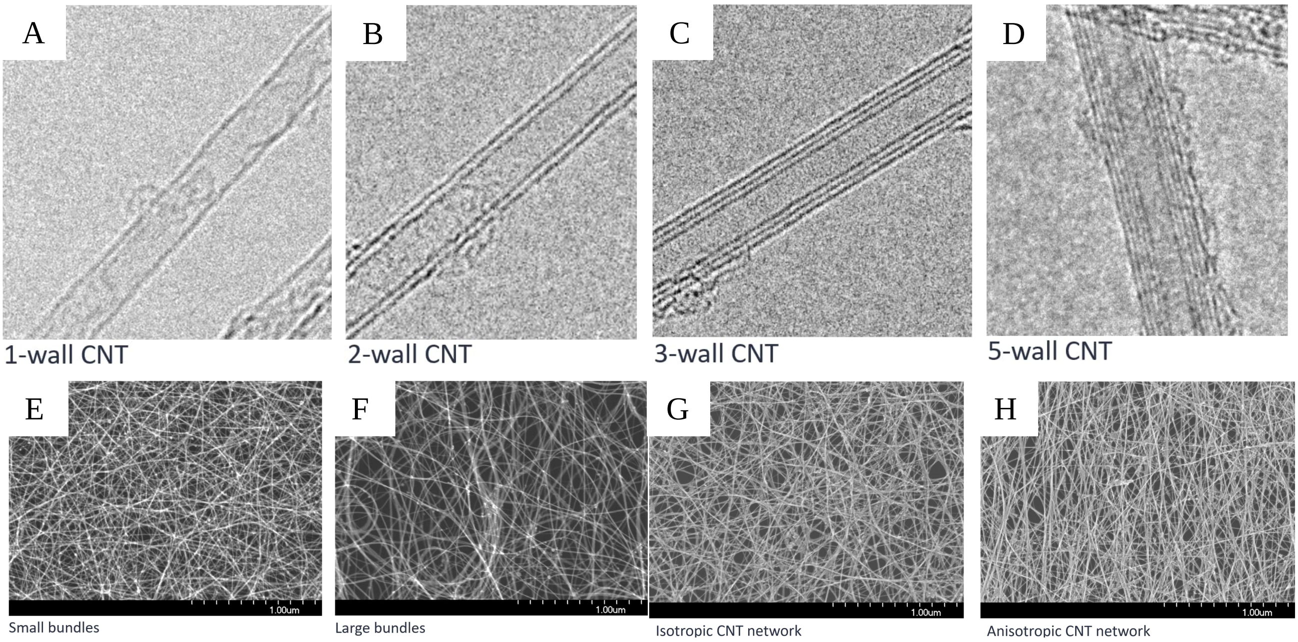

Figure 2. A-D) Transmission electron microscope (TEM) images of carbon nanotubes with different wall counts. E-F) The same amount of CNTs, but in smaller or larger bundles. Alternatively, larger bundles can result in a more durable network with less exposed surface area. G-H) Comparison of an isotropic random CNT network to an oriented anisotropic CNT network.

The practically unrestricted scalability of the direct transfer process allows for very large membrane sizes, or different shapes, as shown in Figure 3. This scalability for example enables the direct fabrication of pellicles exceeding 12 inches, if required by the semiconductor industry.

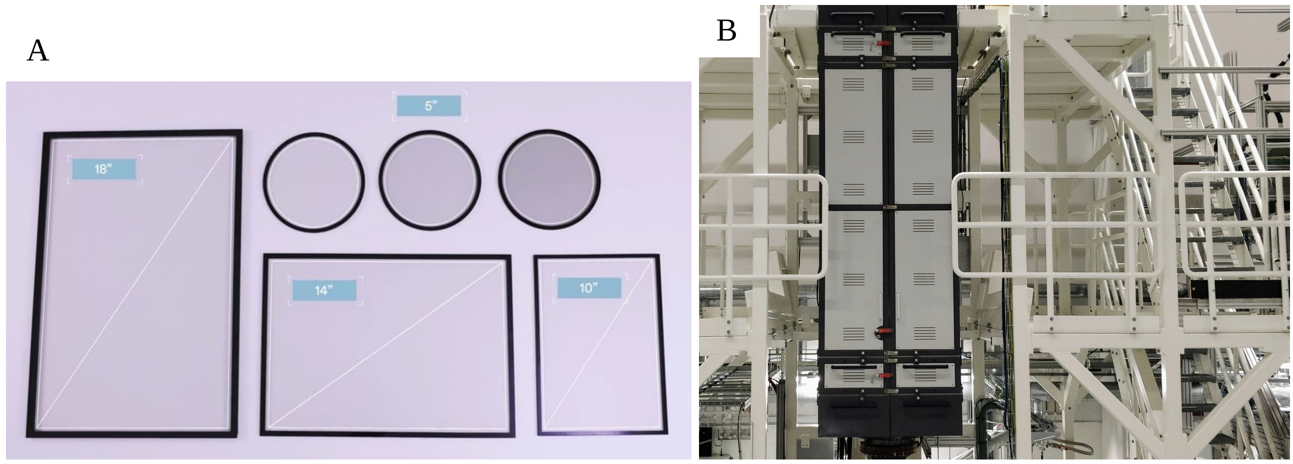

Figure 3. A) Direct deposition of CNT membranes allows for facile fabrication of practically any size, shape, or thickness of freestanding CNT films. B) Vertically mounted Canatu FC-CVD reactor for the synthesis of CNTs.

Carbon nanotubes inherit their physical and chemical properties from graphite and graphene. The high tensile strength of 1-dimensional CNTs makes the 2-dimensional membranes very robust with highly versatile mechanical properties, even allowing some stretching within the membrane to withstand unexpected mechanical loads without breaking or shattering similar to conventional thin film pellicles. In pellicle and debris filtering applications, this elastic and plastic deformability without shattering can help safeguard system integrity in the event of accidents or unforeseen consequences. Analogous to graphite, CNTs have high heat stability, especially in vacuum, where they can withstand extremely high temperatures without breaking or decomposing.

3. POST-PROCESSING

3.1 Purification

High purity of the CNT membrane is often a fundamental necessity. Any outgassing or ejection of material from the pellicle or membrane at high temperatures can damage other components within any EUV machinery. Here we showcase a thermal vacuum purification method, which removes metals and organics from the CNT membrane, as more closely quantified by Rutherford backscattering (RBS) and X-ray photoelectron spectroscopy (XPS) experiments in Table 1. Metal nanoparticles, which are commonly used as catalysts in CNT synthesis, must be thoroughly removed to ensure purity of the manufactured CNT membrane, as shown in TEM pictures in Figure 4. Empty shells can be seen in the TEM images, which contained metal nanoparticles prior to purification. As quantified in Table 1, in addition to metal contaminants being removed, the remaining surface oxygen loading is also remarkably low when compared to typical carbon nanomaterials.[1–4] This further increases EUV transmission, since oxygen absorbs EUV more than carbon.[5]

Table 1. Rutherford backscattering (RBS) and X-ray photoelectron spectroscopy (XPS) results from a purified CNT pellicle of 96 EUV%T.

After purification	RBS (at-%)	XPS (at-%)
Carbon	98.19	98.66
Oxygen	1.78	1.34
Metal catalyst	0.03	0.00

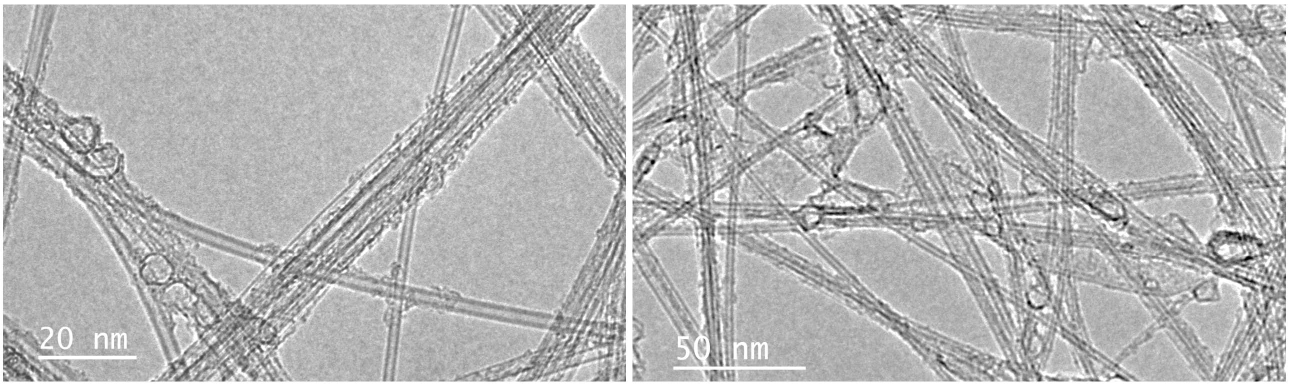

Figure 4. Transmission electron microscopy (TEM) images of purified CNT pellicles, with the metal nanoparticles removed from the graphitic shells.

3.2 Functionalization

Conformality and thickness control of coatings on CNT membranes can be enhanced by engineering the surface chemistry of CNTs to target the specific chemistry used in the ALD, CVD, or even PVD deposition. In practice, this is accomplished by altering or augmenting the surface functional groups on CNTs via wet or dry functionalization post processes. Figure 5 showcases two examples of such functionalization on CNT membranes, as measured by Fourier transform infrared spectroscopy (FTIR).

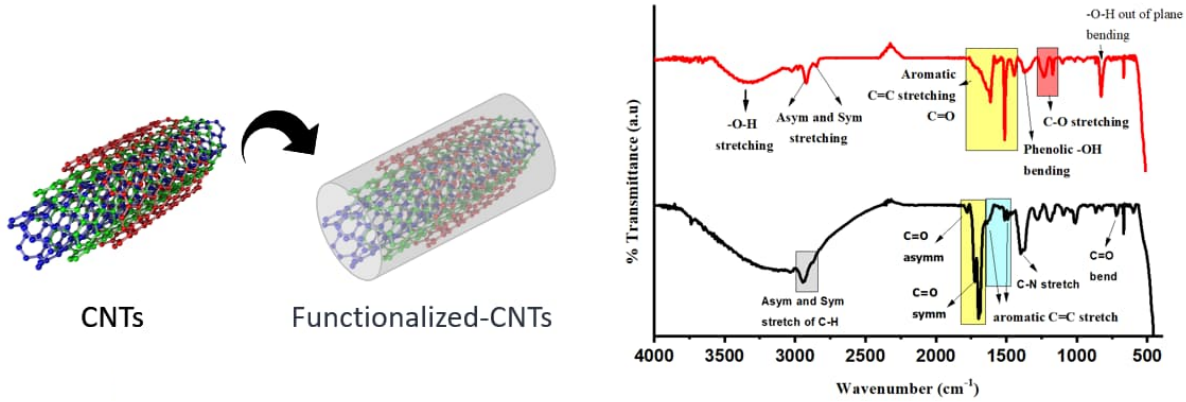

Figure 5. Effect of two different CNT functionalizations, as measured by Fourier transform infrared spectroscopy (FTIR). The top (Red) FTIR spectrum shows a substantial amount of Carbon-Oxygen functionalities, whereas the bottom (Black) spectrum shows a spectrum more predominant in Carbon-Nitrogen bonding.

3.2 Coatings

Coatings can be applied to CNT membranes if case the application, such as debris filtering, requires for example i) optical filtering to remove deep ultraviolet (DUV) photons, or ii) providing a rough gas seal and differential pressure to separate gas compartments in EUV machinery. Conventionally, CNTs can be coated with any PVD, ALD, or CVD coatings, such as Boron Nitride[6], Silicon Carbide, or Boron Carbide to name a few. Here, in Figure 6, we exhibit a novel and more unusual coating method: The electrochemical coating of freestanding CNT membranes. Similar to self-limiting ALD processes, the characteristic mechanisms of electrochemistry enable inherent advantages that allow for enhanced conformality and thickness control in the coating process.

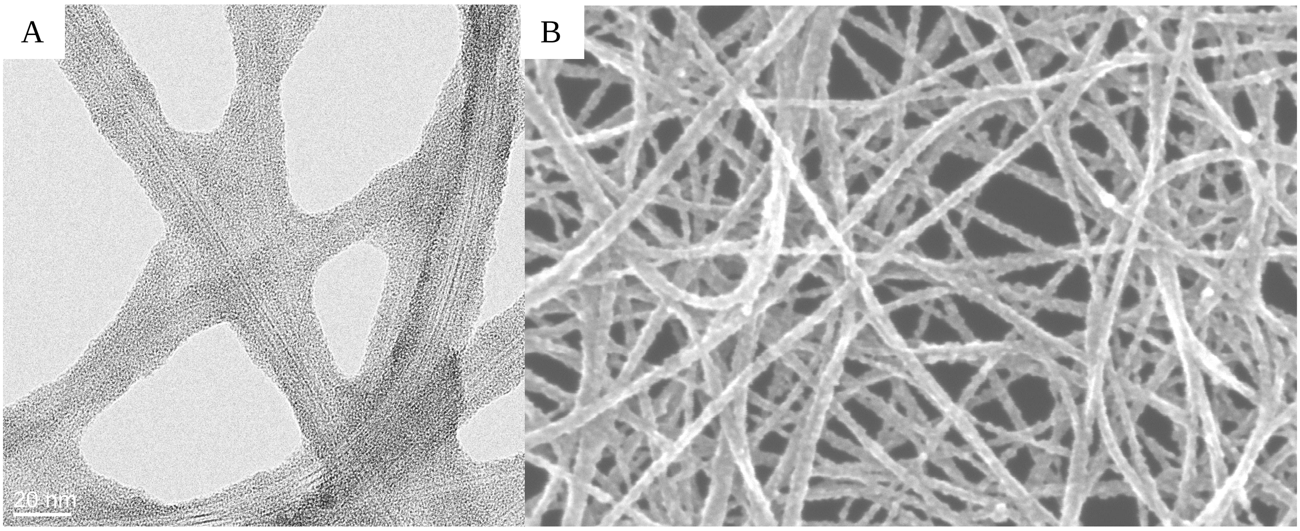

Figure 6. Electrochemical coating of freestanding CNT membranes with high conformality and good thickness control. A) TEM image, and B) SEM image of an electrochemical coating on CNT membrane.

4. APPLICATION EXAMPLE: DEBRIS FILTERING

Due to their exceptional mechanical properties, as discussed in Section 2, CNT membranes are inherently applicable as debris filters to stop particles. In Figure 7, an uncoated CNT membrane was placed directly in front of a pulsed cathodic arc source, equipped with a metal target. This cathodic arc produced plasma and molten metal particles of high kinetic energy, which then hit the CNT membrane at high speed. As shown in the SEM images in Figure 7: the biggest particles have been stopped by the membrane and have recoiled off. There are also some smaller particles that have attached to the membrane. Especially in the larger crater in Figure 7 (A), the CNT membrane has been significantly deformed, as the incoming particle has i) likely entered the film from below where there is a smaller opening, ii) maybe split into smaller pieces as evidenced by the larger upper part of the crater, and iii) exited the crater. Most importantly, it should be noted that even with extensive damage shown, there is no breaking, rupturing, or shattering of the membrane visible.

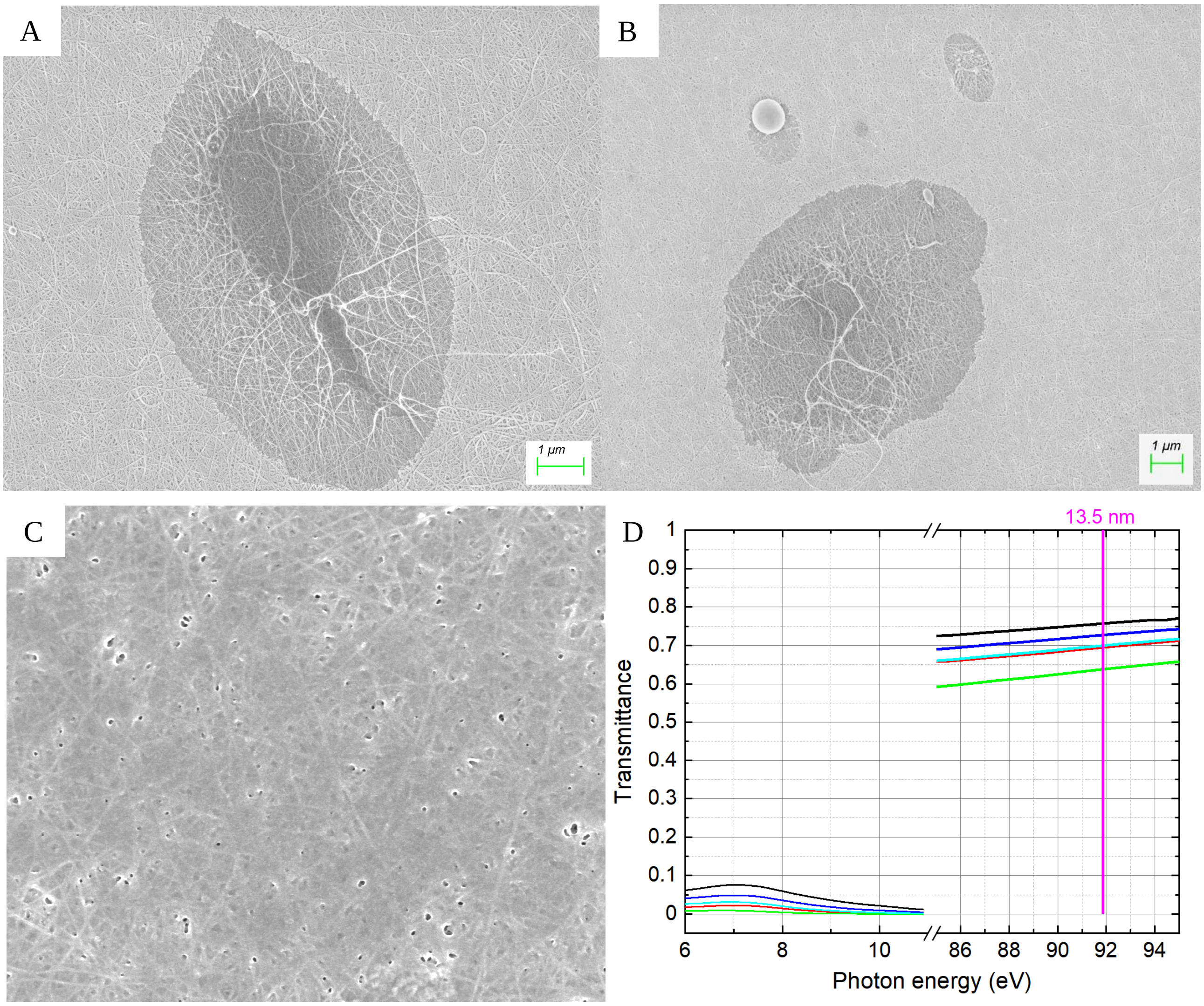

Figure 7. A-B) An uncoated CNT membrane was bombarded by high kinetic energy molten metal particles from a pulsed arc plasma source. The biggest particles have been stopped by the membrane and have recoiled off. High deformability of the membrane is observed, but no visible breaking or rupturing. The apparent broken coating in (A-B) is from the metal plasma. C) SEM image of a novel coating developed for blocking of DUV photons – while letting the EUV photons through. With increased thickness, some levels of gas-seal and differential pressure are also achieved. D) EUV and DUV transmittances of the coating displayed in (C).

As discussed before, debris filter applications might also require specific wavelength filtering. For example, DUV photons can be detrimental to specific mirrors, detectors, or photoresists used in EUV machinery. Figure 7 (D) shows the EUV and DUV transmittances of a coating developed by Canatu for this specific purpose. The transmittance of DUV photons in the energy range from 6 to 11 eV are reduced – while letting the EUV photons through with high transmittance. SEM image in Figure 7 (C) also shows this coating. By varying the thickness of the coating, some levels of gas sealing and differential pressure can also be achieved.

If the CNT membrane is required to allow gases to pass through, a 12 cm in diameter membrane 80 nm thick with a transmittance of 86 %T at 550 nm (94 %T EUV) can handle 100 L/min with a 7.6 Pa differential pressure. Due to this high tolerance to pressure pulses, CNT membranes are ideal for extreme environments found e.g., in vacuum applications.

Lastly, a novel all-carbon mesh structure has been developed to replace conventional metal meshes and is displayed in Figure 8. Manufactured from Canatu CNTs and utilizing the same direct dry deposition as for other CNT membranes, this semi-transparent carbon mesh can be fabricated in practically any size, shape, or thickness, and can be attached to any frame provided. The fabrication process can also be altered to accommodate completely custom and arbitrary mesh designs.

Meshes are commonly used in debris filter or X-ray applications to provide additional mechanical support for the film that is attached to its top surface, and to stop film tear propagation after puncture. Compared to a conventional metal mesh, the CNT mesh advantages include enhanced mechanical properties especially in the film-to-mesh adhesion, as well as excellent tolerance to mechanical vibrations and pressure fluctuations. Additionally, the all-carbon design preserves spectral purity of incoming signals in X-ray applications.

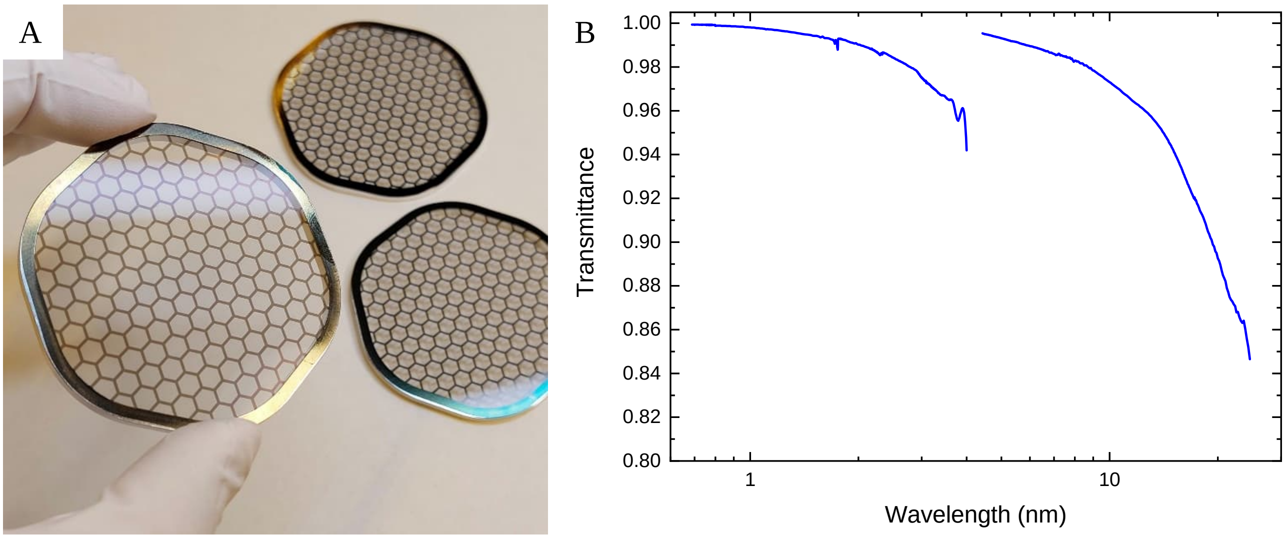

Figure 8. A) A novel all-carbon mesh structure to replace conventional metal meshes. Manufactured from Canatu CNTs using the direct dry deposition methods, the design of this carbon mesh can be fully customized, and applied to any frame provided. B) X-ray transmittance of a typical 96 EUV%T CNT membrane (no mesh).

As investigated together with Ametek Finland Ltd. and University of Palermo, under support from European and Italian space agencies,[7] Canatu CNT membranes have shown applicability in astrophysics space missions as high-performance debris and optical blocking filters for soft X-ray detectors, such as telescope entrance filters and focal plane filters. These optical filters are placed in front of the detector to block particles and photons outside the energy range of interest, while at the same being highly transparent to X-rays and durable enough to handle missions to space. The CNT membranes can endure mechanical pressure and vibration conditions required for a space launch.[7]

4. Conclusions

Here we have demonstrated a simple yet thoroughly customizable fabrication route for scalable CNT membrane mass production: The combination of proprietary FC-CVD reactor synthesis with the direct dry deposition of freestanding CNT membranes. This end-to-end manufacturing process, starting from reagent gases, enables direct control and reproducibility over the final properties of the nanomaterial product. The exceptional mechanical and thermal properties of the CNT membranes, which can endure mechanical pressure and vibration conditions required for a space launch, can be further enhanced with post processing steps, ranging from purification to different coatings. In addition to EUV pellicles, these CNT membranes are also suitable for other roles, such as filtering debris from an EUV source, blocking DUV photons and electrons, or providing a gas seal for differential pressure. The remarkable versatility of this CNT membrane material platform can adapt to the stringent application requirements of the future EUV lithography and semiconductor industry.

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