

# Application of Plasma Etching and Surface Treatment in 2D and 1D Materials Research

## Introduction

Two-dimensional (2D) materials (like graphene and transition metal dichalcogenides) and one-dimensional (1D) nanomaterials (such as carbon nanotubes) have extraordinary electronic and mechanical properties stemming from their reduced dimensionality. Realizing their potential in applications – from nanoelectronics to sensors – requires precision in processing: removing contamination, tailoring surfaces, and patterning structures without destroying intrinsic properties. Vacuum plasma etching and plasma surface treatment have emerged as indispensable tools in this realm. These techniques use low-pressure glow discharges of gases to generate reactive ions and radicals that can clean, etch, or functionalize material surfaces with fine control. Tabletop radio-frequency (RF) plasma systems (for example, the Tergeo series by PIE Scientific) are commonly employed in research labs for these tasks, offering flexibility in process power, gas chemistry, and mode of operation. Indeed, numerous studies on 2D/1D materials explicitly cite the use of such plasma cleaners for device fabrication and treatment steps. This article reviews how vacuum plasma processes are applied to exfoliation, etching, and surface modifications of 2D and 1D materials. We discuss the underlying mechanisms by which plasma exposure alters these nanomaterials (through physical sputtering, chemical functionalization, removal of residues, etc.), and we survey common plasma gases ( $O_2$ , Ar,  $CF_4$ ,  $N_2$ ,  $H_2$ ) and their specific roles. Specific examples from recent literature – including cases where **Tergeo** plasma systems were used – highlight the state-of-the-art. Our focus is on how controlled plasma treatments enable researchers to prepare clean interfaces, pattern nanomaterials with nanometer precision, and tune surface chemistry, all while mitigating damage in these atomically thin or narrow structures.

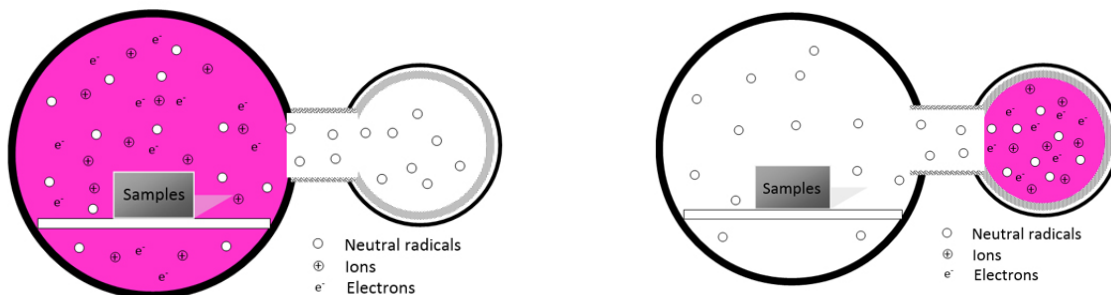
## Plasma Treatment Mechanisms

Plasmas interact with materials via a combination of physical and chemical pathways. **Physical etching** occurs when energetic ions (from the plasma) bombard the surface, knocking out atoms (sputtering) without necessarily reacting chemically. For example, an argon RF plasma provides a stream of  $Ar^+$  ions that can dislodge weakly bound surface atoms or adsorbates purely by momentum transfer. **Chemical effects** arise from neutral radicals and reactive ionic species that react with surface atoms to form volatile products or to attach functional groups. In an oxygen plasma, reactive oxygen radicals ( $O\cdot$ ) readily attack hydrocarbon residues, oxidizing them into  $CO$ ,  $CO_2$ , and  $H_2O$  that desorb from the surface. In addition, UV photons generated in the plasma can break molecular bonds at the surface. The balance between physical and chemical effects is tunable by the choice of gas and plasma parameters.

**Direct vs. downstream plasma:** Plasma systems can be configured so that the sample is either directly in the glow discharge or located downstream, separated from the discharge by a gap or mesh. In direct mode, the sample is subjected to both the full flux of ions and radicals; this maximizes etch rate but can easily damage delicate nanomaterials. In downstream (remote) mode, only neutral radicals (and diffuse UV) reach the sample, as ions recombine or are stopped before hitting the surface. Downstream plasma thus performs gentler chemical treatment with minimal ion

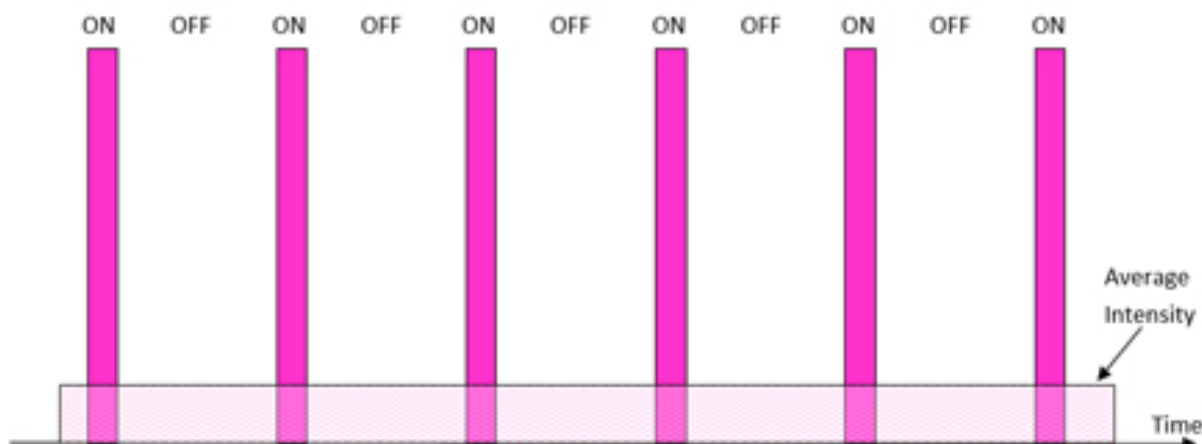


bombardment. This has proven crucial for treating 2D materials that are only a few atoms thick. For instance, in one study a *gentle remote* O<sub>2</sub> plasma (1 min at 10 W) was applied to an hBN-covered 2D heterostructure using a Tergeo plasma cleaner, creating surface functionalization that enabled uniform ALD coating without physically etching the underlying layers. The remote plasma introduced reactive –OH groups on the hBN surface for ALD seeding, while preserving the integrity of the WSe<sub>2</sub>/MoS<sub>2</sub> layers below – a task that would be far more damaging under direct plasma exposure.



Direct mode plasma processing (left) vs remote/downstream mode plasma processing (right)

**Continuous and Pulsed Plasma:** Modern plasma tools, like Tergeo series plasma systems made by PIE Scientific LLC, often allow pulsing of the RF power to modulate the duty cycle of the discharge. By using short “on” bursts separated by “off” periods, the average plasma density and ion energy can be drastically reduced compared to continuous operation. The Tergeo systems, for example, can operate in pulsed mode with duty cycles <1% (at ~500 Hz frequency), yielding an extremely weak plasma that is almost invisible but still effective in surface cleaning. This fine control over plasma intensity – spanning orders of magnitude – allows researchers to find a process window that removes undesired layers or contaminants while leaving the target material essentially unscathed. In practice, a high-power continuous plasma might be used for rapid etching of bulk contaminants or resist, whereas a low-power pulsed plasma is used for final cleaning or functionalization of a fragile 2D crystal.



Continuous and pulsed plasma

**Synergistic etch processes:** By combining gases or sequential plasma steps, one can achieve etching behavior that neither gas alone could accomplish. A striking example is the controlled thinning of multilayer MoS<sub>2</sub> by alternating oxidizing and reducing plasmas. In a recent approach, an O<sub>2</sub>/SF<sub>6</sub> plasma (providing O and F radicals) was first used to oxidize/fluorinate the MoS<sub>2</sub> surface, and then an H<sub>2</sub> plasma step was applied. The hydrogen plasma does not itself etch MoS<sub>2</sub>, but instead passivates newly created sulfur vacancies by terminating them with H, and it scavenges leftover F radicals as HF gas. This prevents uncontrollable continued etching at defect sites. By repeating this two-step cycle (30 s H<sub>2</sub> passivation, 15 s O<sub>2</sub>/SF<sub>6</sub> etch), researchers removed about 10 layers of MoS<sub>2</sub> per cycle in a layer-by-layer fashion. The hydrogen step effectively self-limits the damage by “capping” reactive sites, illustrating how plasma chemistry can be choreographed to achieve high precision in material removal. Such digital etching strategies blur the line between exfoliation and etching – enabling thinning of a flake down to a few layers or even a monolayer with nanometer accuracy, something difficult to do by mechanical exfoliation alone.

## Applications in 2D Materials

Plasma processes have become integral to many aspects of 2D material research, from initial exfoliation and cleaning to device fabrication and chemical modification.

**Exfoliation and thinning:** While mechanical exfoliation (the Scotch tape method) is the go-to for obtaining single-layer flakes, plasma etching provides a complementary approach to thin down multilayer samples in a controlled manner. As described above, carefully dosed O<sub>2</sub> or CF<sub>4</sub>-based plasmas can trim layers from TMD crystals. Pure oxygen plasma tends to etch MoS<sub>2</sub> and similar dichalcogenides at defect sites and edges, often leading to pit formation or slow isotropic erosion. By introducing a passivation step (e.g. H<sub>2</sub>), or using mild plasma conditions, one can achieve more uniform thinning. This has enabled the

fabrication of ultrathin photodetectors and tunnel junctions from thicker exfoliated flakes by plasma trimming. In essence, plasma etching serves as a nanoscale “sandpaper” to exfoliate layers that are difficult to peel off otherwise. Additionally, plasma treatments can intentionally create nanopores in 2D membranes: for example, helium ion plasma or O<sub>2</sub> plasma can drill pores in monolayer graphene or MoS<sub>2</sub> for filtration and sensing applications (though often an electron beam or ion beam is used for atomic precision). Plasma-drilled nanopores in 2D materials have been explored for DNA sequencing devices, although controlling the pore size with plasma alone remains challenging compared to ion beam sculpting.

**Lithographic patterning:** Perhaps the most common use of plasma etching in 2D materials research is defining device structures. After a 2D material is transferred or grown on a substrate, photolithography or electron-beam lithography is used to mask certain regions (e.g., with resist), and then an oxygen or fluorine-based plasma etches away exposed areas of the 2D material. This technique has been used to carve graphene into narrow ribbons, to separate one large 2D film into many devices, or to etch mesas and channels in TMD materials for transistors. Oxygen plasma is highly effective at rapidly etching graphene because it reacts with carbon to form gaseous oxides; graphene patterns with ~100 nm resolution have been achieved by O<sub>2</sub> plasma etching through a resist mask. For MoS<sub>2</sub> and other TMDs, fluorine-containing plasmas (SF<sub>6</sub>, CF<sub>4</sub> often with O<sub>2</sub> added) are commonly employed to anisotropically etch straight-edged patterns, since these plasmas can break the Mo–S bonds and form volatile MoF<sub>6</sub> and SF<sub>x</sub> or SO<sub>x</sub> species. For instance, source/drain regions of few-layer MoS<sub>2</sub> transistors have been plasma-etched to isolate channel areas, and nanopatterns in WS<sub>2</sub> or black phosphorus have been realized via plasma etching for nanoelectronics. One study preparing Hall-effect measurement structures in monolayer MoS<sub>2</sub> reported plasma-etching the MoS<sub>2</sub> for 1 minute in a Tergeo cleaner (49 W RF, Ar/O<sub>2</sub> ambient) to define the device geometry. The ability to etch with a mixture of inert and reactive gas (Ar plus a trace of air in that case) illustrates how researchers tune plasma chemistry to achieve a controllable etch – the Ar ions provide sputtering while the O<sub>2</sub> (from air) oxidizes the material, preventing redeposition.

**Removing residues and contaminants:** 2D materials are extremely sensitive to surface contamination. Residues from polymer-based transfer (e.g., poly(methyl methacrylate) used to transfer CVD graphene) or from lithography (e.g., resist films) often remain on the surface and can degrade device performance by scattering charge carriers or altering contact resistance. Plasma cleaning is a straightforward way to remove these organic residues. A brief low-power O<sub>2</sub> plasma exposure can “ash” away remnant organic films, leaving a cleaner 2D surface. For example, after transferring graphene to a target substrate, researchers sometimes use an O<sub>2</sub> plasma clean (perhaps 10–30 s at 10–50 W) to burn off PMMA residue instead of (or in addition to) solvent rinsing. The key is to use mild conditions so as not to etch the graphene itself: graphene’s carbon lattice will also oxidize if overexposed to O<sub>2</sub> plasma. Using a downstream O<sub>2</sub> plasma mode is one way to mitigate direct ion damage during this cleaning. In addition to organic removal, plasma can eliminate adsorbed water layers and other adventitious adsorbates, yielding a fresh surface for subsequent processing. In the context of device assembly, plasma cleaning is often applied just before steps like metal deposition or dielectric coating to ensure good adhesion. Thakur *et al.* (2023) found that an oxygen plasma treatment on a SiN<sub>x</sub> substrate dramatically improved the priming of an adhesion layer (HMDS) by generating –OH groups on the surface. Although in that case the substrate (SiN<sub>x</sub>) was plasma-treated, the result was better stability for the 2D MoS<sub>2</sub> membrane transferred onto it. This highlights that plasma cleaning isn’t only for the 2D material itself but also for any interface in contact with it (substrates, electrodes, etc.), which in turn influences the 2D material’s behavior.

**Surface functionalization and chemical modification:** Plasma treatments can deliberately modify the surface chemistry of 2D materials, imparting new functionalities. In graphene, exposing the lattice to different plasmas can introduce various dopants or functional groups. An O<sub>2</sub> plasma, for instance, adds

oxygen functional groups (forming graphene oxide regions with C–O–C epoxides, C–OH, C=O groups) which makes the graphene surface hydrophilic and chemically reactive. Such oxidation, however, comes at the cost of converting  $sp^2$  carbon to  $sp^3$  bonds, degrading electrical conductivity. Nitrogen plasmas ( $N_2$  or  $NH_3$ ) can incorporate nitrogen into graphene, yielding  $sp^2$  carbon with substitutional N (graphitic or pyridinic N sites) or surface amine groups – effectively n-doping the graphene and also improving its chemical sensing affinity for certain molecules. Unfortunately,  $N_2$  plasma can cause damage similar to  $O_2$  plasma if not carefully controlled, as both tend to create vacancies and break the aromatic network. One study noted that direct  $O_2$  or  $N_2$  plasma functionalization of graphene severely degraded its carrier mobility, prompting researchers to devise alternative approaches. One approach is to use a *sacrificial* layer: Shin *et al.* and Nourbakhsh *et al.* employed an  $O_2$  plasma on a sacrificial graphene layer, which was later peeled off or served as a buffer to protect the main graphene underneath, allowing ultrathin ALD dielectrics to be deposited on graphene without directly exposing it to plasma. Another approach is to use gentler plasmas like hydrogen. **Hydrogen plasma functionalization** of graphene has been shown to be reversible: a short exposure to  $H_2$  plasma will hydrogenate the graphene (adding C–H bonds, which opens a bandgap and increases resistance), but subsequent annealing at  $\sim 400^\circ C$  can desorb the hydrogen and restore the pristine  $sp^2$  carbon network. Karasulu *et al.* demonstrated that by using a 35 s  $H_2$  plasma pretreatment on graphene, they could achieve uniform nucleation of ALD  $Al_2O_3$  films (down to 8 nm thick) on the graphene, and then by annealing the sample they largely recovered the graphene's original conductivity. In contrast, a 30 s  $O_2$  plasma pretreatment, while also enabling ALD growth, irreversibly damaged the graphene's mobility due to persistent oxygen functional groups. Thus, hydrogen plasma provided a means to “chemically prime” the graphene surface for coating without permanently sacrificing its electronic quality. Beyond graphene, other 2D materials can also be functionalized: for instance, plasma treatments have been used to intentionally create sulfur vacancies in  $MoS_2$  (which can serve as catalytic sites or points for bonding molecules), or to incorporate oxygen into  $MoS_2$  to form  $MoS_{2-x}O_x$  alloys. Fluorination of 2D materials is another avenue –  $CF_4$  plasma exposure can add F atoms to a  $MoS_2$  or graphene surface, which has been explored as a way to modify surface energy and electronic structure (fluorographene is an insulator analogous to Teflon). However, heavy fluorination by plasma typically renders a conducting 2D material insulating by breaking its conjugation, so such methods are used when insulation or extreme surface functionalization is desired.

## Applications in 1D Materials

One-dimensional nanomaterials, especially carbon nanotubes (CNTs), have likewise benefited from plasma processing techniques for purification, functionalization, and device integration. Multi-walled and single-walled CNTs often come with impurities (residual catalyst particles, amorphous carbon) or are coated with surfactants when dispersed in solution. Plasma cleaning can effectively burn off amorphous carbon and organic residues from CNTs. For example, oxygen plasma is commonly used to purify CNTs by oxidizing away the non-tubular carbon and leaving graphitic tubes intact (graphitic carbon has a higher resistance to oxidation compared to disordered carbon). This must be done carefully – overly aggressive  $O_2$  plasma can also damage the CNTs themselves, creating defects or even etching the tubes into shorter fragments.

**Tip opening and cutting:** Oxygen plasma is particularly useful for opening the caps at the ends of carbon nanotubes, which is important for certain applications (like filling nanotubes or attaching functional groups at the ends). The ends of as-grown CNTs are often closed shells of carbon; a brief  $O_2$  plasma can etch away these cap structures, effectively unsealing the nanotube and creating open pores at the tips. This increases the accessible surface area of CNTs and can improve their performance in, say, electrochemical

applications (by allowing electrolyte access into the inner walls of tubes). It also creates carboxyl or carbonyl groups at the opened ends, which are useful for chemical derivatization. In fact, O<sub>2</sub>-plasma-treated CNT fiber electrodes have shown enhanced capacitance and better wettability due to the introduction of oxygen functional groups. If instead the goal is to shorten CNTs (cutting long tubes into shorter segments), plasma etching can be employed in combination with mechanical agitation – for example, exposing CNTs in solution to an Ar/O<sub>2</sub> plasma while ultrasonically vibrating can cut them. Alternatively, CF<sub>4</sub>/O<sub>2</sub> plasma has been used to etch and shorten CNT arrays with some directional control.

**Sidewall functionalization:** Plasma discharges enable **covalent functionalization** of CNT sidewalls without the need for aggressive wet chemistry (which often requires strong acids). Different gas plasmas introduce different functionalities: an NH<sub>3</sub> or N<sub>2</sub> plasma can add nitrogen moieties (amine, amide, or even substitutional N in the carbon lattice), O<sub>2</sub> plasma adds oxygenated groups (hydroxyl, carbonyl, carboxyl), and CF<sub>4</sub> or SF<sub>6</sub> plasma can attach fluorine atoms to the carbon framework. Each of these modifications alters the surface chemistry of the CNTs. For instance, N/O plasma-treated CNTs show improved dispersion in polar solvents and enhanced bonding to polymer matrices, which translates to stronger CNT-polymer nanocomposites. The introduced polar groups improve interfacial interactions with epoxy resins in composite materials, as noted by Ghorannevis *et al.* in a study on plasma-functionalized CNT/epoxy composites (2018). Similarly, nitrogen-functionalized CNTs can provide specific chemical affinity: one report found that plasma-aminated CNTs had a higher capacity for ammonia gas adsorption, as the basic amine sites could bind acidic NH<sub>3</sub> molecules, improving sensor response. Fluorination via CF<sub>4</sub> plasma is a way to alter the electronic structure of CNTs – attaching fluorine makes the CNT more insulating and can open a bandgap, but it also makes the surface highly electronegative. Fluorinated CNTs are sometimes used as an intermediate: the C–F bonds can later be replaced by other functional groups via chemical substitution, allowing a two-step functionalization route (plasma fluorinate, then substitute F with, say, thiol or azide by solution chemistry).

**Plasma-assisted alignment and integration:** In some cases, plasmas have been used to modulate the charge on CNTs or nanowires to assist in aligning them or bonding them to surfaces. A mild O<sub>2</sub> plasma can make CNTs more hydrophilic, which aids in depositing them evenly from a solution onto substrates (as the tubes won't clump from hydrophobic interactions as much). Moreover, plasma-treated CNTs have been used as interconnects and via fills in microelectronics – an O<sub>2</sub> plasma not only cleans them but also activates substrate surfaces to improve contact.

As with 2D materials, the *gentleness* of the plasma process is key. Multi-walled CNTs can sustain more plasma exposure than single-walled CNTs (since only the outer wall might be damaged while inner walls remain intact). Nonetheless, optimizing power and time is crucial to achieve the desired functionalization level without destroying the 1D structure. Researchers often characterize plasma-treated CNTs with techniques like X-ray photoelectron spectroscopy (XPS) to quantify the new functional groups, and Raman spectroscopy to monitor structural damage (an increase in the D-band indicates more defects). For example, plasma oxidation of CNTs leads to clear XPS peaks for oxygen functionalities and a moderate rise in the Raman D/G ratio, whereas plasma nitridation would show N1s XPS signals. A controlled plasma treatment thus achieves a balance: introducing enough defects for functionality, but not so many as to completely disrupt conduction along the nanotube.

## Common Process Gases and Their Effects

Different plasma gases have characteristic effects on 2D/1D materials, and the choice of gas is a crucial handle in tailoring the process outcome. Below we summarize the commonly used gases ( $O_2$ , Ar,  $CF_4$ ,  $N_2$ ,  $H_2$ ) and their roles:

- Oxygen ( $O_2$ ):** Oxygen plasma is widely used for its strong chemical reactivity with organic materials and many chalcogenides. It produces atomic oxygen and ozone that oxidize most exposed surfaces. For carbon-based materials (graphene, CNTs),  $O_2$  plasma can effectively remove organic contaminants by burning them off as  $CO/CO_2$ . It also readily reacts with the carbon lattice itself, attaching oxygen functional groups or etching away carbon to form volatile oxides. This makes  $O_2$  plasma a go-to for cleaning and for defining patterns (etching) in graphene. However, the damage to lattice structure is significant if not controlled – oxidation converts  $sp^2$  bonds to  $sp^3$  and creates vacancies, severely reducing electrical conductivity. In TMD materials like  $MoS_2$ ,  $O_2$  plasma alone etches predominantly by reacting at defect sites and physically dislodging sulfur (which can form  $SO_2/SO_3$ ). Pure  $O_2$  etching of  $MoS_2$  tends to yield slower, somewhat disorderly material removal (unless combined with another gas). In summary,  $O_2$  plasma is excellent for removing organics and introducing oxygen-containing functional groups, but it must be used briefly or at low power when preserving a pristine lattice is important.
- Argon (Ar):** Argon is an inert gas, so an Ar plasma etches materials by physical sputtering rather than by chemical reaction. High-energy  $Ar^+$  ions can knock atoms out of a surface lattice, essentially sandblasting it on the atomic scale. Ar plasmas are thus useful for general surface cleaning of metals and inorganic materials where chemical oxidation is not desired. In 2D materials, Ar alone can induce defects (e.g., sputtering S atoms from  $MoS_2$ , or carbon atoms from graphene) without passivating those vacancies (since Ar doesn't stick). This can lead to vacancy defect creation. Ar plasma is often used in combination with  $O_2$  or other gases – for example, an Ar/ $O_2$  mixture in an RF plasma cleaner provides both sputtering and oxidizing action. The Ar component helps to dislodge any surface layer or break through a resist film, allowing oxygen to penetrate and react more effectively. In practice, Ar plasmas are also popular for gentle cleaning of TEM grids with 2D material samples, because a low-power Ar downstream plasma can remove adsorbates while inflicting minimal chemical change. When precision milling of a 2D material is needed (to cut a very narrow trench, for instance), Ar ion beams or plasmas are often employed because they can physically sputter with directional control under bias. One must be cautious that Ar sputtering can amorphize a crystal surface if overdone.
- Tetrafluoromethane ( $CF_4$ ) and other fluorinated gases:**  $CF_4$  is a commonly used fluorine source in plasma etching. In a plasma,  $CF_4$  dissociates to produce fluorine radicals ( $F\cdot$ ) and various  $CF_x$  fragments. Fluorine atoms are highly reactive with many materials: they readily form stable fluorides with metals and semiconductors (e.g., converting Si to  $SiF_4$  gas). In 2D materials,  $CF_4$  or  $SF_6$  plasmas are extremely useful for etching robust materials like h-BN or  $MoS_2$  that are less affected by pure  $O_2$ . For instance, adding a small fraction of  $O_2$  to a  $CF_4$  plasma dramatically increases the etch rate of molybdenum, as the combination produces both F and O that can respectively form volatile  $MoF_x$  and  $SO_x$  species. This principle is used to plasma-etch  $MoS_2$  with  $CF_4/O_2$  or  $SF_6/O_2$ : sulphur is oxidized and removed, and Mo is fluorinated and removed, effectively volatilizing the  $MoS_2$ . Fluorine plasma can also directly fluorinate carbon materials. Fluorine atoms attach to graphene or CNT sidewalls forming C–F bonds (semi-ionic or covalent). Highly fluorinated graphene ( $CF_x$ ) becomes an insulator and is sometimes called “fluorographene” – it's analogous to graphene oxide in that it's an insulator derived from graphene, but with fluorine instead of oxygen. Fluorination of CNTs increases their electrical

resistance and makes them more insulating, but can be useful for subsequent chemical derivatization (as mentioned earlier). Notably, fluorocarbon plasmas tend to deposit a thin polymeric film of fluorocarbon on surfaces if there is not enough oxygen present to scavenge the carbon. Thus,  $\text{CF}_4$  plasma etching of, say, resist or plastics often requires adding  $\text{O}_2$  to prevent polymer buildup. In the context of 2D/1D materials,  $\text{CF}_4/\text{O}_2$  or  $\text{SF}_6/\text{O}_2$  plasmas provide a highly anisotropic, fast etch and are used when vertical sidewalls or efficient material removal is needed (such as defining the shape of a  $\text{MoS}_2$  transistor or cutting through a thick h-BN flake).

- Nitrogen ( $\text{N}_2$ ):** Nitrogen plasmas generate atomic nitrogen and some excited nitrogen molecules that can interact with surfaces in several ways. With carbon materials, nitrogen can incorporate to form C–N bonds; for example, plasma post-treatments have been used to nitrogen-dope graphene and CNTs (introducing pyridinic, pyrrolic, or graphitic nitrogen functionalities). N doping can modulate the electronic properties (often making graphene more  $n$ -type) and improve electrochemical performance (nitrogen sites can act as catalytic centers or improve wettability).  $\text{N}_2$  plasma alone is somewhat less aggressive at etching carbon than  $\text{O}_2$  plasma – it may create defects without fully etching away the carbon backbone, which can be beneficial for doping purposes. Additionally,  $\text{N}_2$  plasma can nitride certain materials; for example, plasma nitridation of silicon or of metal surfaces is a known technique. In 2D materials, there is research into using  $\text{N}_2$  or  $\text{NH}_3$  plasmas to convert  $\text{MoS}_2$  to  $\text{MoN}_x$  or to dope TMDs with nitrogen, although these are less common than oxidation or fluorination approaches. A mixed  $\text{N}_2/\text{O}_2$  plasma (sometimes called an air plasma) will introduce both N and O functionalities on carbon nanotubes, and has been shown to greatly improve the performance of CNT/epoxy composites by adding polar amide and carboxy groups that bind with the polymer matrix. In summary,  $\text{N}_2$  plasmas are chiefly used for doping and functionalization rather than for bulk etching. One must keep in mind that nitrogen-based functionalization still creates defects in graphene/CNTs (as the N typically substitutes or terminates where a C was), so similar to oxygen, it can degrade conductivity if overdone. But moderate exposure yields a useful balance: for instance, a nitrogen plasma treatment can make a CNT sensor more sensitive to certain gas molecules by providing specific binding sites, even though the CNT's baseline resistance might increase slightly due to introduced defects.
- Hydrogen ( $\text{H}_2$ ):** Hydrogen plasma has a unique role as a reducing and passivating agent. Atomic hydrogen from a plasma can reduce metal oxides (by stripping oxygen and forming  $\text{H}_2\text{O}$ ) and can also terminate dangling bonds with hydrogen atoms. In processing 2D materials,  $\text{H}_2$  plasma is valued for its ability to passivate defects without heavy functionalization. As discussed,  $\text{H}_2$  plasma on graphene results in hydrogenation (formation of C–H bonds), but importantly this process is reversible – an anneal can remove the H, effectively healing the lattice. This makes  $\text{H}_2$  plasma an attractive option for temporary functionalization or cleaning. For example, if one wanted to remove oxygen groups or other adsorbates on a graphene surface, a forming gas plasma ( $\text{H}_2/\text{N}_2$ ) can be used to gently reduce the surface, potentially improving graphene's conductivity by healing some oxide-induced p-doping. In  $\text{MoS}_2$  and TMDs,  $\text{H}_2$  plasma interacts primarily by bonding to unsaturated sulfur or metal sites. It has been shown to passivate sulfur vacancies in  $\text{MoS}_2$ , meaning the hydrogen terminates the dangling bonds of undercoordinated Mo at vacancy sites. This prevents those sites from acting as nucleation points for oxide growth or further etching. Consequently,  $\text{H}_2$  plasma by itself causes negligible etching of  $\text{MoS}_2$  – in fact, experiments observed essentially *no* thickness loss in  $\text{MoS}_2$  under a pure  $\text{H}_2$  plasma, in stark contrast to  $\text{O}_2$  plasma which does etch. Instead, hydrogen simply saturates the edges/defects and then leaves once the sample is taken out or annealed.  $\text{H}_2$  is also known to react with fluorine; thus in a mixed gas plasma (like  $\text{CF}_4/\text{H}_2$  or  $\text{SF}_6/\text{H}_2$ ), the hydrogen can form HF, which is volatile, effectively removing fluorine and any bound species. This is leveraged in cyclical processes to protect certain phases as mentioned earlier. Beyond carbon and TMDs,  $\text{H}_2$  plasma can hydrogenate other 1D/2D materials (for example, converting semiconducting black phosphorus to

phosphine gas in a degradative process, or hydrogenating monolayer boron nitride to attach N–H and B–H). In semiconductor manufacturing, H<sub>2</sub> plasma or forming gas plasma is often used to passivate interface defects (such as silicon dangling bonds) – a concept that could be applied to 2D material interfaces as well (like H-passivating the interface between a 2D material and a substrate or dielectric). Overall, hydrogen plasma is considered a gentle tool to neutralize reactive sites and even *repair* materials to some degree, complementing the more aggressive oxidative and fluorinating plasmas.

## Summary and Outlook

Vacuum plasma etching and surface treatment techniques have become cornerstones of advanced 2D and 1D materials research. They provide the capability to clean delicate atomic layers, pattern structures at the nanoscale, and chemically modify surfaces in ways not achievable by wet chemistry alone. Crucially, plasma processes operate in a dry and often room-temperature environment, compatible with ultra-high vacuum and cleanroom workflows, which is ideal for device fabrication sequences involving 2D materials. The versatility of plasma tools – exemplified by systems like PIE Scientific’s Tergeo series that offer direct/downstream and continuous/pulsed modes in one instrument – allows researchers to tailor plasma exposure from extremely gentle to highly aggressive, depending on the task. This flexibility is important because 2D and 1D materials span a range from fairly robust (multi-layer graphene can sustain some plasma etch) to very fragile (single-layer phosphorene will oxidize away in minutes if not careful). By tuning plasma conditions, as well as selecting appropriate gases, scientists can now routinely process these materials with sub-nanometer precision.

Looking forward, the application of plasma treatments is poised to expand in both scope and sophistication. On the one hand, as researchers explore new 2D materials (such as magnetic monolayers, ferroelectric thin films, or novel 2D polymers), plasma methods will need to be developed to handle their unique chemistries. For example, gentle plasma doping could be a way to modulate the properties of 2D magnets without large-scale chemical substitution, or plasma could be used to pattern 2D covalent-organic frameworks that are otherwise hard to etch. On the other hand, even for well-studied materials like graphene and CNTs, plasma processing is being refined to achieve ever better control. In situ diagnostics (like optical emission monitors or mass spectrometry of the plasma species) now provide feedback to precisely end-point the etch or functionalization process. This means one can stop a plasma treatment exactly when a monolayer is reached or when a certain level of functionalization (judged by emission intensity of a fragment) is achieved, improving reproducibility.

Another important future direction is plasma-based synthesis and post-treatment. Plasma-enhanced chemical vapor deposition (PECVD) already grows graphene and CNTs; similarly, plasma treatments can heal defects in 2D materials (plasma annealing under H<sub>2</sub> or forming gas) or even stitch together 2D heterostructures by activating the interface. With the rise of large-scale 2D material production (like wafer-scale graphene and MoS<sub>2</sub>), there is industrial interest in plasma etching for device patterning and plasma surface functionalization for integrating these materials into semiconductor process flows. The challenge will be to ensure that plasma processes remain gentle enough not to introduce unacceptable damage or variability – a lesson well appreciated in the research community, where studies often report the need for careful plasma calibration for each new material system.

In conclusion, plasma etching and surface modification provide a powerful toolbox for advancing 2D and 1D materials science. By mastering these techniques – understanding how oxygen vs. hydrogen plasma affects a given material, or how to exploit a machine’s downstream mode to avoid ion damage –

researchers can engineer nanomaterials and interfaces with a high degree of control. The continued innovation in plasma equipment and methodology, guided by feedback from the 2D/1D materials community, will undoubtedly yield new capabilities, such as even more selective reactions or damage-free processing. This synergy between plasma physics and materials science is enabling the next generation of nano-devices and heterostructures that harness the remarkable properties of 2D and 1D materials.

## References

1. Okamura, H. *et al.* Air-stable and efficient electron doping of monolayer MoS<sub>2</sub> by salt-crown ether treatment. **Nanoscale** **13**, 9638–9646 (2021).
2. Thakur, M. *et al.* High durability and stability of 2D nanofluidic devices for long-term single-molecule sensing. **npj 2D Mater. Appl.** **7**, 11 (2023).
3. Wang, P. *et al.* Detecting and controlling DNA translocation through a nanopore using a van der Waals heterojunction diode. **Nano Lett.** **23**, 1010–1019 (2023).
4. Snure, M. *et al.* Two-dimensional BN buffer for plasma enhanced atomic layer deposition of Al<sub>2</sub>O<sub>3</sub> gate dielectrics on graphene field effect transistors. **Sci. Rep.** **10**, 14699 (2020).
5. Karasulu, B. *et al.* Uniform atomic layer deposition of Al<sub>2</sub>O<sub>3</sub> on graphene by reversible hydrogen plasma functionalization. **Chem. Mater.** **29**, 9532–9540 (2017).
6. Ebrahimejad, H. *et al.* Controlled plasma thinning of bulk MoS<sub>2</sub> flakes for photodetector fabrication. **ACS Omega** **5**, 30290–30298 (2020).
7. Ghorannevis, Z. *et al.* Role of nitrogen–oxygen plasma functionalization of carbon nanotubes in epoxy nanocomposites. **Polymer Compos.** **39**, E1133–E1141 (2018).
8. Yamada, T. *et al.* Plasma functionalization of carbon nanotubes for the capture of ammonia molecules. **Plasma Process. Polym.** **19**, e2200018 (2022).