CHEMICAL SPUTTERING STUDIES OF LITHIATED ATJ GRAPHITE

BY

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THESIS

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ABSTRACT
Plasma Facing Component (PFC) materials are crucial to fusion reactor development. There is no one material that functions as an ideal PFC material. As a result, coatings are applied to control the interaction between plasmas and the PFC material. Lithium wall conditioning treatments in the National Spherical Torus Experiment have shown dramatic improvements in plasma performance. In order to understand the complex system of lithiated ATJ graphite, chemical sputtering measurements of plain and lithiated ATJ graphite have been conducted in IIAX (Ion-surface InterAction eXperiment) facility. Chemical sputtering of graphite is dependent on the ion energy and substrate temperature, hence the total effects of treating ATJ graphite with lithium in hydrogen plasma are investigated in terms of different target temperatures and bias voltages. The dominant chemical sputtering product is Methane (CH₄). It was found that lithium treatments have suppressed the chemical sputtering of ATJ graphite. The suppression of chemical sputtering effect as function of varying lithium thickness on ATJ graphite has been thoroughly studied. The experimental data suggests that the thickness of the lithium has to be greater than the surface roughness of the ATJ graphite to see substantial suppression in chemical sputtering.
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Chapter 1 : INTRODUCTION

The Plasma Facing Components (PFC) mainly consists of "First wall" and "Divertor". PFC material choice is one of the most challenging problems faced by the nuclear fusion community. Several materials have been considered in the past; however, there is no consensus on the ideal PFC material [1]. The surface of the PFC material is subjected to erosion by energetic ions and neutral atoms escaping from the plasma [2]. Plasma facing components (PFC) suffers from high-energy particle bombardment, radiation and heat flux which lead to backscattering, outgassing, sputtering etc. The impurities from these processes diffuse back to the core plasma leading to loss of energy through Bremsstrahlung radiation, excitation and ionization [3]. The divertor has to withstand heat flux of ~20 MW/m² [4]. A lot of research has been done to find a material that can survive and still not degrade plasma performance [5, 6].

High Z materials such as tungsten and molybdenum show promise, as their sputtering yields from D⁺ and T⁺ are relatively low [7]. Even small traces of these elements in the core plasma cause plasma energy losses through inelastic collisions and direct radiative processes with plasma electrons [8]. Tungsten has very low sputter yield but its large atomic number and self-sputtering cause problems in a fusion reactor [9]. Some low Z materials such as graphite have been proposed as an alternative to the high Z materials.
1.1 Graphite as a PFC

Graphite is the most popular choice for PFC. Graphite PFCs have been used in TFTR, Doublet III, JET and NSTX. Graphite has superior thermomechanical properties [10] but it suffers from chemical erosion due to hydrogen plasma exposure and radiation enhanced sublimation, which lead to net erosion [11] and tritium retention problems. Graphite has low outgassing, low Z, and capability of handling high heat fluxes [12]. NSTX uses high performance isotropic ATJ graphite for its divertor and other plasma facing components.

Graphite erodes by bombardment with light ions H\(^+\), D\(^+\). The reactivity of graphite with energetic hydrogen ions and thermal hydrogen atoms results in the formation of methane and the enhanced erosion yield relative to physical sputtering [13]. Carbon-based materials are prone to problems. Oxygen can etch carbon efficiently forming CO and CO\(_2\) which are loosely bound to the carbon surface. At low temperature plasmas, chemical erosion of the carbon surface by low energy hydrogen ion impact leads to the ejection of light hydrocarbon molecules, which plays a major role in determining the carbon based- material lifetime [14].

1.2 Chemical sputtering of graphite

Sputtering of graphite is major problem in graphite PFC as it leads to core plasma dilution and other undesirable effects. Graphite can be eroded by physical and chemical sputtering mechanisms. Physical sputtering of graphite involves ejection of lattice carbon atoms leading to erosion for hydrogenic impact energies above \(\sim 40\) eV
[15]. This physical sputtering process does not depend on the temperature of the graphite.

Chemical sputtering is defined as a process whereby ion bombardment causes or allows a chemical reaction to occur which produces a particle that is weakly bound to the surface and hence easily desorbed into the gas phase [16]. Chemical sputtering has a strong temperature dependence significantly below melting or sublimation temperatures [17]. Chemical erosion of carbon by hydrogen is a thermally activated process which does not require energetic species whereas chemical sputtering is a process whereby ion bombardment causes or allows a chemical reaction to occur which produces a particle that is weakly bound to the surface and easily desorbed into the gas phase [18]. Chemical sputtering includes all three basic erosion mechanisms like chemical erosion, physical sputtering, and chemical sputtering [13]. It is not clear as to which mechanism dominates as their extent of influence depends on experimental parameters like ion energy and temperature of the graphite.

The chemical sputtering of graphite by hydrogen ions is a complex process depending on surface temperature, ion flux, surface state of the material, and energy of the incident particles [13]. These parameters show strong interdependence [13]. Chemical sputtering of graphite results in the production of methane, ethane, propane, etc. The most dominant chemical erosion product is methane. Temperature dependence and energy of incident particles is the two most relevant parameters for this work so they will be discussed in the coming sections. Hydrocarbon formation by chemical sputtering is preceded by surface-damage creation and amorphization,
and occurs by H-passivation of the dangling bonds thus produced [28].

1.2.1 Chemical sputtering dependence on graphite temperature

Graphite temperature dependence has been studied in great detail in the past. Figure 1 summarizes the results of methane production as a function of time in a pyrocarbon sample using a remote mass spectrometer.

![Figure 1 - Theoretical and experimental equilibrium methane formation rates during H\(^+\) → pyrocarbon. −− Theory, \(Q_1 = 38\) kcal, \(Q_2 = 54.6\) kcal, fitted to \(T_{\text{m}}\) \(\sigma = 10^{-16}\) cm\(^2\), \(J_o = 10^{15}\) cm\(^2\) s\(^{-1}\). −−−−−− Experimental [19].](image)

From Figure 1, it can be seen that the CH\(_4\) production increases with increasing graphite temperature. It reaches a maximum around 900 K and then decreases for further increasing temperatures. Yamada et al. published similar results with a maximum yield occurring around maximum temperature \(T_{\text{max}} = 800\) K [20]. The occurrence of a maximum yield for chemical sputtering with energetic hydrogen ions at \(T_{\text{max}}\) was assumed to result from the competition of an exponential increase of the
reaction rate between carbon and hydrogen with an even stronger decrease of the hydrogen concentration in the surface at temperatures exceeding 800 K and at lower temperatures the lattice concentration of hydrogen saturates and the reaction rate increases with increasing temperature, while at higher temperatures the recombinative hydrogen release decreases the hydrogen content so that the reaction rate decreases [13].

1.2.2 Chemical sputtering dependence on incoming ion energy

Chemical sputtering strongly depends on the incident ion energy. Figure 2 summarizes the results of methane production yield as a function of impinging hydrogen ion energies on different pyrolytic graphite samples. The curves have a maximum at 1000eV and the yield decreases on further increasing the ion energies.

![Figure 2 - Methane production yield as a function of ion energy for hydrogen ions impinging on pyrolytic graphite measured at different sample temperatures [20].](image-url)
Roth et al. [21] have shown that the maximum of the energy dependence shifts to lower energy with decreasing temperature. The shape of the energy dependence curve was found to be identical to physical sputtering, hence the similar knock on effects of physical sputtering was assumed to be responsible for chemical sputtering mechanism [13]. Chemical erosion yield is not dramatically decreased for ion energies below the threshold for physical sputtering [22].

1.3 Chemical sputtering detection method

There are several ways to detect chemical sputtering: weight loss measurements, mass spectroscopy, ellipsometry, optical emission spectroscopy, cavity probes and multiple beam experiments. Mass spectroscopy method will be discussed in the coming section, as it is most relevant to this work.

1.3.1 Mass spectroscopy

A remote mass spectrometer on the reaction chamber is the most popular chemical sputtering detection mechanism. Chemical erosion species measured in the remote mass spectrometer could have been formed at wall areas by reflected projectiles instead of at the target itself. High methane production from the walls of the reaction chamber is a major problem in these types of experiments. The reaction chamber walls can act like a sink wherein the methane can stick to the walls of the chamber. Chemical sputtering species reach the remote mass spectrometer after many wall collisions, hence they are stable.

Mass spectrometer measures the partial pressures of these stable chemical sputtering
species that reach the ionizer of the mass spectrometer. Mass spectrometers allow
real time analysis of the chemical sputtering species. Determination of chemical
sputtering species involves careful data analysis and interpretation. Sensitivity of the
mass spectrometer has to be calibrated for the chemically sputtered species. Usually
stable gases are used for this purpose [32, 33]. When molecules of a gas are struck
by energetic electrons they cause ionization and fragments of several mass-to-charge
ratios are created. The mass-to-charge values are unique for each gas species and the
peak amplitudes are dependent on the gas and instrumental conditions [34]. This
pattern of fragments is called a cracking pattern. For identification of a gas mixture,
their cracking patterns overlap, so the measured mass spectra have to be decomposed
into the individual contributions. Solving a system of linear equations is the most
popular analysis technique.

A line-of-sight mass spectrometry is used to reduce the contribution of wall species
to the contribution of target species. Even if the mass spectrometer has a line of sight
to the surface of interest, the signal is dominated by the wall species. A line-of-sight
setup is necessary but not sufficient to detect reactive species and significant effort
has to be spent to reduce the signal contribution from recycling species [13].

1.4 ATJ graphite

NSTX uses ATJ graphite tiles as its primary PFC material. ATJ graphite is type of
graphite manufactured by UCAR Carbon Company. ATJ graphite is a polycrystalline,
fine grain, high strength material which can be machined to precise tolerances and a
fine surface finish. ATJ graphite has high thermal shock resistance due to the combination of low thermal expansion, high thermal conductivity and low elastic modulus [28].

1.5 Lithium coatings on PFC

There is no one material that serves as an ideal PFC, hence coatings are applied to coatings are applied to control the interaction between plasmas and the surrounding material. Lithium wall conditioning is the most popular wall conditioning method in fusion reactors. Lithium is a low Z material which offers huge benefits like low recycling, high edge temperatures, improved plasma confinement, suppressing ELMs, enhances plasma performance, etc. [23]. Lithium dramatically reduces hydrogen recycling, oxygen, and carbon plasma impurities [24]. Experiments on the NSTX have shown the benefits of solid lithium coatings on carbon PFC’s to diverted plasma performance in both L and H- mode confinement regimes. Better particle control, with decreased inductive flux consumption, and increased electron temperature, ion temperature, energy confinement time, and DD neutron rate were observed. Increased lithium coverage resulted in the complete suppression of ELM activity in H-mode discharges [25].

1.5.1 Properties of lithium

Lithium is an alkaline metal with atomic number of 3 with a single valance electron. Since they can easily give up this electron, they form cat-ions. Due to this property of
lithium, it is a good conductor of heat and electricity. Lithium is a highly reactive element, though the least reactive among the alkali metals. Lithium occurs in nature as $^6\text{Li}$ and $^7\text{Li}$ which are two stable isotopes with 3 and 4 neutrons respectively. The isotopic abundance of $^6\text{Li}$ is 7.5% and $^7\text{Li}$ is 92.5%. The most important properties are listed in Table 1.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>3</td>
</tr>
<tr>
<td>Element category</td>
<td>Alkali Metal</td>
</tr>
<tr>
<td>Group, period, block</td>
<td>1,2,s</td>
</tr>
<tr>
<td>Standard atomic weight</td>
<td>6.941(2)</td>
</tr>
</tbody>
</table>
| Electron con
guration | $1s^2 2s^1$ |
| Phase | Solid |
| Atomic Radius | 152 pm |
| Density | 0.534 g·cm$^{-3}$ |
| Liquid density at melting point | 0.512 g·cm$^{-3}$ |
| Boiling Point | 1615 K, 1342 °C, 2448 °F |
| Melting Point | 453.69 K, 180.54 °C, 356.97 °F |
| Critical point | (extrapolated) 3223 K, 67 MPa |
| Heat of fusion | 3.00 kJ·mol$^{-1}$ |
| Heat of vaporization | 147.1 kJ·mol$^{-1}$ |
| Molar heat capacity | 24.860 J·mol$^{-1}$·K$^{-1}$ |
| Electronegativity | 0.98 (Pauling scale) |
| Oxidation states | +1,-1 |
| Covalent radius | 128±7 pm |
| Van der Waals radius | 182 pm |
| Ionization energies | 1st: 520.2 kJ·mol$^{-1}$ (5.392eV) 2nd: 7298.1 kJ·mol$^{-1}$ (75.638eV) 3rd: 11815.0 kJ·mol$^{-1}$ (12.451eV) |
| Crystal Structure | Body centered cubic |
| Magnetic ordering | Paramagnetic |
| Electrical resistivity | (20 °C) 92.8 nΩ·m |
| Thermal conductivity | 84.8 W·m$^{-1}$·K$^{-1}$ |
| Thermal expansion | (25 °C) 46 μm·m$^{-1}$·K$^{-1}$ |
| Young’s modulus | 4.9 GPa |
| Shear modulus | 4.2 GPa |
| Bulk modulus | 11 GPa |

Table 1 - Properties of Lithium [36]
1.6 Lithiated graphite

Alkali metals intercalate into graphite [26]. Lithium, being an alkali metal, readily intercalates into graphite forming a lithium-graphite matrix. This intercalation of lithium onto graphite occurs even at room temperature. Lithium on the surface diffuses into the graphite quickly, but a small fraction of lithium still remains on the surface.

J.R. Dahn et al. [27] have explained the three basic stages behind the lithium intercalation behavior. In the first stage, one lithium atom can intercalate for every six graphite atoms forming LiC₆. In stage two, weakly bound lithium resides in cavities. Lithium hydride is not formed and it is unclear as to how lithium interacts with the hydrogen. In the third stage, lithium intercalates in between sheets of carbon thereby resulting in two layers of lithium for each carbon sheet [27]. There is no observable boundary layer between lithium and graphite, due to which lithium thickness on to graphite cannot be determined with precision. Since we cannot get an accurate estimate of the thickness, we can estimate equivalent thickness using a Silicon witness plate. When the top lithium layer is sputtered away, a lithium layer will be formed immediately by the diffusion of underlying lithium towards the surface [29]. A single monolayer of lithium coating is much more chemically and thermally stable than bulk 2 to 3 monolayers or more of lithium. A multi-monolayer coating would be subject to evaporation, oxidation and sputtering, and the liberated lithium would enter the plasma as neutrals [31].
1.6.1 Hydrogen interaction

Removal of hydrogen and oxygen impurities is a desirable quality of an ideal PFC. Removal of hydrogen impurities is called as hydrogen pumping. These hydrogen impurities degrade the performance of the DT fuel. Chemical activity of a fresh lithium layer accounts for the hydrogen pumping effect by forming lithium hydride (LiH) and for the oxygen gettering effect by forming lithium oxide (Li2O). It has been observed that hydrogen enhances lithium diffusion on graphite surfaces [29]. Li atoms bind in the vicinity of H atoms, but it is unlikely that bulk lithium hydride (LiH) could be formed in graphite [27]. The presence of H atoms increases the lattice spacing of graphite, which leads to enhanced diffusion of lithium on graphite [30]. If the graphite contains hydrogen impurities they will lead to deeper lithium diffusion. Hence, a helium glow discharge has to be carried out to remove hydrogen impurities to get a good coverage of lithium on graphite [29].

1.7 Suppression of physical sputtering of graphite due to lithium wall coating

Previous studies have shown that lithium coating on graphite show a reduction of net sputtering yield of graphite. Figure 3 is a plot of physical sputtering yield of lithium coated graphite as a function of magnetron sputtering time in a helium discharge. It can be seen from Figure 3 that with increasing the lithium dose, suppression of sputtering is more enhanced and lasts for longer time [35]. It can be observed from Figure 4, that the sputtering yield decreases with increasing the lithium dose. A uniform one monolayer of lithium coating significantly suppresses the physical
sputtering of the underlying material [31]. A thin lithium layer on graphite was found to reduce both physical sputtering in a helium plasma and chemical sputtering, and LiOH is more easily desorbed than H₂O [31]. It is believed that the thin monolayer of lithium on the surface of the graphite is the key for suppression of sputtering.

**Figure 3** - Physical sputtering yield of lithium coated isotropic graphite as a function of magnetron sputtering time for a helium discharge [35]

**Figure 4** - Normalized sputtering yield at the sputtering time t=2min as a function of lithium dose expressed by film thickness. Closed circles denote C yield and open circles (C + Li) yield [35].
1.8 Suppression of chemical sputtering of graphite due to lithium wall coating

Lithium conditioning effect on graphite has been well studied in the past, and it has been observed that graphite wall conditioning by in situ lithium deposition resulted in significant suppression of carbon impurities in TFTR [38]. There are several mechanisms by which lithium suppress graphite sputtering. The mechanisms are (1) direct masking of graphite surfaces with lithium layer, (2) formation of Li-C chemical bonding at the interface, and (3) reduction of hydrogen flux onto walls as a consequence of low hydrogen recycling induced by lithium deposition [39]. H. Toyoda et al. [39] reports that lithium layer suppresses the methane yield by ~ 25% compared to bare graphite surfaces and no methane will be released if the graphite surfaces is completely covered by lithium. They further add that graphite surfaces are so rough that lithium evaporation does not fully mask the graphite surfaces thereby exposing bare shadow regions that include porous and micro-channels.

Figure 5 - Time evolution of methane yield from CFC (carbon fiber-reinforced carbon composite) at 300 K after hydrogen glow ignition [37].
H. Yagi et al. [37] reports that in order to obtain a full effect of lithium intercalation, preconditioning of Li-deposited surface is necessary as it suppresses chemical erosion of graphite completely. Lithium atoms strongly react with water vapor and most of the molecules get adsorbed on the graphite surface, hence lithium containing impurity layers will be formed during the lithium deposition. It can be observed from Figure 5 that methane yield at 300K is almost completely suppressed after sufficient hydrogen glow conditioning. It is believed that hydrogen glow conditioning removes oxygen impurities from the graphite surface, which allows the intercalated lithium atoms to diffuse towards the surface. Furthermore, it has been hypothesized that hydrogen glow discharge inserts hydrogen atoms in the graphite layer, so the chemical interaction may take place between the hydrogen atoms and the intercalated lithium atoms [37].

1.9 Objective of this work

NSTX uses ATJ graphite and carbon fiber composite tiles as its primary plasma facing component [40]. Sputtering of first wall material is an unavoidable process for impurity release in tokamaks [44]. Chemical sputtering of graphite is presently one of major carbon impurity sources in high flux divertor machines [45]. Previously, the Ion Surface Interaction Experiment (IIAX) at the University of Illinois [41–43] has reported thermal evaporation and physical sputtering studies of ATJ graphite and lithiated ATJ graphite. The details of the chemical interaction during chemical sputtering are not well understood, and so far, there is no reliable theory. Their
behavior is complex and not understood easily. Unlike physical sputtering there is no good theoretical model for chemical sputtering [46]. Hence, a detailed chemical sputtering studies of lithiated ATJ graphite as a function of lithium thickness is necessary for finding out the minimum thickness of lithium layer that is needed in a fusion reactor to completely suppress chemical sputtering of graphite, as well as to understand the complex system of lithium-carbon-hydrogen chemistry. Majority of the previous studies on chemical sputtering were done using ion beam irradiation in the steady state. This approach greatly simplifies the experiment but does not reflect the actual conditions seen in a tokamak. To simulate such conditions, this work uses transient low energy plasma conditions. This work will focus on measuring the suppression of chemical sputtering of ATJ graphite due to lithium application as a function of varying lithium thickness on ATJ graphite.
Chapter 2 : EXPERIMENTAL SETUP

2.1 Modified Ion-Surface InterAction eXperiment (IIAX) design

The actual experimental set-up consists of two chambers, the IIAX chamber where the actual chemical sputtering reactions take place and the remote sampling chamber where the line of sight MSRGA (Magnetic Sector Residual Gas Analyzer) is attached to monitor the reaction species. MSRGA is the main diagnostic tool used in this work. Most RGAs cannot operate above $\sim 10^{-4}$-$10^{-5}$ Torr range. During the plasma, the pressure inside the chamber is $\sim 10^{-3}$ Torr range, hence a differential pumping chamber is used to reduce the pressure to a workable range of the RGA. Figure 6 is a picture of the chambers.

![Figure 6 - Photograph of the chambers](image)

IIAX was modified to perform the chemical sputtering measurements of lithiated ATJ graphite in low temperature plasma. The IIAX main chamber is a right cylinder of 610 mm (24’’) inner diameter and 356mm (14’’) inner height. The IIAX
chamber is pumped by Alcatel 5900CP turbo molecular pump with a pumping speed of 900 l/sec backed by a Dayton rotary vane roughing pump. The ultimate base pressure of the IIAX chamber is in the order of $\sim 2 \times 10^{-8}$ Torr.

The remote sampling chamber is 3-way conflate tee flange which is pumped by Leybold TURBOVAC 361 turbo pump with a pumping speed of 345 l/s. The Leybold turbo pump is backed by a Welch rough pump. The ultimate base pressure of the remote sampling chamber is in the order of $\sim 2 \times 10^{-8}$ Torr. Both the chambers roughing line have gas traps to protect the chambers from back streaming of oil vapor from their respective rough pumps. Back streaming of oil vapor can cause a strong interference with the actual chemical sputtering measurements from the target, hence it is necessary to install oil traps in such experiments.

The remote sampling chamber is connected to the IIAX chamber using a sniffer tube with an orifice. The orifice is very critical for differentially pumping and that is where the line of sight sputtering products enter the sampling chamber and eventually makes it to the MSRGGA. The sniffer tube is installed in IIAX chamber in such a way that it is line of sight, close to the target surface and also underneath the coil to capture the reaction products efficiently without capturing much from the chamber wall reactions.

This upgraded IIAX RF facility has the flexibility of doing ion beam as well as plasma based experiments. An internal RF coil is installed to do the plasma based experiments. The internal IIAX set-up consists of a stainless steel RF coil, a movable cylindrical ATJ graphite target of 2.5 cm diameter, an in-situ lithium evaporator. The
ATJ graphite target is connected to the heating and biasing circuitry. The ATJ graphite target is mounted in such way that the target can be translated along a line to different positions. The target can also be rotated to expose the plain ATJ surface or lithiated ATJ surfaces to the sniffer tube which allows direct comparison of both sides with the same background. Contributions from three different positions of the target were evaluated and the positions are ATJ graphite side under the coil facing the sniffer, lithiated ATJ graphite side under the coil facing the sniffer and the target assembly totally retracted to the walls of the chamber away from the line of sight of the sniffer tube. Figure 7 shows upgraded IIAX chemical sputtering detection set-up.

![Figure 7 - Schematic of the IIAX chemical sputtering detection set-up.](image)

Thermocouple and biasing connections are attached to the target to monitor the temperature and bias the target. The ATJ graphite target is heated by means of “Joule heating” where a huge current is passed through it to release heat. A step
down transformer and a variac is used for this purpose. The variac is connected to the step down transformer which is in turn connected to the ATJ graphite through a stainless steel feed through. Figure 8 shows the target heating set-up.

![Figure 8 - Photograph of the target heating set-up](image)

All the components are situated within the IIAX chamber so there is need for breaking vacuum. Hence, this type of set-up enables us to get exact quantitative measure of chemical sputtering suppression due lithium. Plasma is ignited in the main chamber using RF antenna coil when the pressure in the main chamber reaches the mTorr range with the hydrogen gas flow. To maintain a constant gas flow during all experiments, a mass flow controller was used to regulate the flow of hydrogen into the chamber. Figure 9 is the photograph of the inside of the IIAX chamber showing the relative positions of various components.
2.2 Residual Gas Analyzer (RGA)

A mass spectrometer is one of the most popular methods in measuring chemical sputtering. An advantage of mass spectrometry is that it produces real-time data and allows measuring parameter variations in much shorter times. A differentially pumped low-mass-sensitive Magnetic Sector Residual Gas Analyzer (MSRGA) is used in this study to track the chemical sputtering products. Line-of-sight setup is necessary but not sufficient to detect reactive species and that significant effort has to be spent to reduce the signal contribution of recycling species from the background [17]. A VTI AV-ODY-EEC magnetic sector RGA is used in this study. The MSRGA is operated in electron multiplier mode for this study with electron impact ionization carried out at the electron energy of 70 eV. The MSRGA is advantageous over the quadrupole RGA in certain aspects. MSRGA has high reliability, high stability, excellent quantitative capability and field maintainability.
Magnetic sector mass spectrometers is very precise in analyzing extreme low masses such as Hydrogen and Helium because of a lack of a "zero blast" effect, which plagues quadrupoles and also because of greater resolution than quadrupoles. The flight tube of a magnetic sector instrument is "field free", it is much less susceptible to contamination [47]. MSRGA allows monitoring masses 1 and 2 which are of significance to this study. Figure 10 is the photograph of the MSRGA that was used in this study.

![Figure 10 - Photograph of our MSRGA](image)

**2.3 Lithium evaporator setup**

The lithium evaporator set-up consists of a tungsten filament and boron nitride crucible. The whole set-up is mounted on a stainless steel tower. The purpose of the stainless tower is to provide the right height for the lithium evaporation to the ATJ graphite target. Lithium foil is loaded onto the boron nitride crucible under Argon environment to prevent the oxidation of lithium. A variac is used to pass current
through the tungsten filament to heat the crucible containing lithium. A thermocouple is installed to the crucible to monitor the temperature of the crucible. Typically the crucible is heated to ~450°C to evaporate lithium. Figure 11 is the photograph of our lithium evaporator set-up.

Figure 11 - Photograph of lithium evaporation setup
Chapter 3: EXPERIMENTAL DETAILS AND DATA

ANALYSIS

3.1 Step 1: MSRGA cracking pattern generation

The first and foremost step in doing chemical sputtering experiments is to generate cracking patterns of various interfering gases at our MSRGA. When molecules of a gas are struck by energetic electrons they cause ionization and fragments of several mass-to-charge ratios are created. The mass-to-charge values are unique for each gas species and the peak amplitudes are dependent on the gas and instrumental conditions [34]. This pattern of fragments is called a cracking pattern. They form a fingerprint that may be used for absolute identification of gases. For example, methane gas will crack in the RGA at peaks 1, 2, 12, 13, 14 and 15 corresponding to \( \text{H}^+ \), \( \text{H}_2^+ \), \( \text{C}^+ \), \( \text{CH}^+ \), \( \text{CH}_2^+ \) and \( \text{CH}_3^+ \) respectively. Cracking pattern of gases depend on the type of the RGA used, location of the RGA, purity of the gas analyzed, detection mode (Electron Multiplier or Faraday Cup) of the RGA, purity of the analyzer filament and the sensitivity of the RGA. The cracking pattern ratios from RGA don’t necessarily have to follow the ratios/patterns given in the NIST (National Institute of Standards and Technology) website. Hence, it very important to generate cracking of various gases that may interfere with the cracking patterns of the gases that is of interest to us. Due to all these reasons, cracking patterns of various gases are obtained for our MSRGA according to our set-up and experimental conditions.

Before doing any experiment, a MSRGA scan of the base line condition of the
chamber is recorded. This is very helpful in subtracting out the background. Varying specific amounts of gases are let in to the IIAX chamber and their cracking ratios at MSRGA are recorded. The background signals can be subtracted to get actual cracking pattern of the gases that are let in to the chamber. The matrix formed from these cracking pattern ratios are used to find the actual partial pressures of the species considered in the data analysis of this work. These experiments are preformed multiple times so that the mean and the standard deviations for each of the component coefficients are established which is then used for data analysis and error propagation. Cracking patterns of methane, hydrogen, water vapor, oxygen, nitrogen, argon and carbon dioxide are generated. These specific gases are chosen because of their interference with the methane cracking pattern. Table 2 shows the cracking pattern matrix with standard deviations from our cracking pattern analysis.

<table>
<thead>
<tr>
<th>Mass</th>
<th>CH&lt;sub&gt;4&lt;/sub&gt;</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>N&lt;sub&gt;2&lt;/sub&gt;</th>
<th>O&lt;sub&gt;2&lt;/sub&gt;</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Ar</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.182 ± 0.028</td>
<td>0.486 ± 0.006</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.087 ± 0.078</td>
</tr>
<tr>
<td>2</td>
<td>0.182 ± 0.028</td>
<td>0.486 ± 0.006</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.456 ± 0.388</td>
</tr>
<tr>
<td>3</td>
<td>0.007225</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.456</td>
</tr>
<tr>
<td>12</td>
<td>0.013 ± 0.002</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.152 ± 0.001</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>0.025 ± 0.001</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>0.182 ± 0.025</td>
<td>0.133 ± 0.007</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>0.203 ± 0.017</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>0.203 ± 0.017</td>
<td>0</td>
<td>0</td>
<td>0.229 ± 0.017</td>
<td>0.246 ± 0.004</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>0.013 ± 0.006</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>0</td>
<td>0.013 ± 0.006</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.379 ± 0.003</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.017</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>28</td>
<td>0</td>
<td>0.866 ± 0.007</td>
<td>0</td>
<td>0.092 ± 0.001</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>32</td>
<td>0</td>
<td>0</td>
<td>0.770 ± 0.017</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.620 ± 0.003</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>44</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.490 ± 0.002</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2 - Cracking pattern matrix of different gases

For example, methane cracks at masses 1, 2 and 12 to 16 and nitrogen cracks at 14 and 28. Hence, the partial pressure at peak 14 has contribution from methane as well as nitrogen. In order to de-convolute the signals and find the contribution of the desired species, it is essential that we consider all the interfering species in the
analysis. A more detailed description on how this de-convolution is performed to get the actual partial pressure of the desired species is presented later in this chapter.

Figures 12-18 show that cracking pattern spectrums generated of various gases.

![Figure 12 - Cracking pattern spectrum of Argon](image1)

![Figure 13 - Cracking pattern spectrum of Methane](image2)
Figure 14 - Cracking pattern spectrum of carbon-di-oxide

Figure 15 - Cracking pattern spectrum of hydrogen
Figure 16 - Cracking pattern spectrum of water.

Figure 17 - Cracking pattern spectrum of nitrogen
3.2 Step 2: Oxygen-Argon plasma cleaning of the chamber

IIAX chamber is made out of stainless steel, which is an alloy of carbon, so it could be a major contributor of carbon in these experiments. The rough pump is an oil sealed rotary vane pump so, there is chance that some of the hydrocarbon pump oil may back stream in to the chamber, in spite of having an oil trap. The back streamed pump oil can be adsorbed to the chamber walls or can reside in the micro cracks of the chamber acting as a source of carbon. Figure 19 is the base line scan of the IIAX chamber before and after Oxygen-Argon plasma cleaning. The peaks 39, 41, 43, 55 and 57 (higher order hydrocarbons) are caused by mechanical pump oil back streaming into the vacuum chamber.
In order to reduce the background carbon contribution, high power argon/oxygen plasma cleaning is performed in the IIAX chamber before the start of the experiments. It can be clearly seen from Figure 15 that the oxygen-argon plasma cleaning helps to get rid of the background carbon contribution. We can observe that the pump oil peaks have come down significantly. The oxygen radicals combine with the hydrocarbons to form carbondioxide (peak 44) and carbon monoxide (peak 28) which can be pumped out with gate valves fully open for a few fours.

3.3 Step 3: Lithium evaporation

ATJ target is placed far away from the lithium evaporator to avoid lithium evaporation on to the target during heating of the crucible. Lithium foil is loaded into the boron nitride evaporator crucible in an argon environment before pumping down
the chamber for performing the experiments. The lithium is evaporated by passing a current through the tungsten filament that encircles the crucible. Variac supplies the current that is need to heat the filament. The temperature of the boron nitride crucible is monitored using a thermocouple. The variac is slowed dialed up so the thermocouple reads ~450°C. The temperature of the evaporator cup is maintained around 450°C for 10 minutes to get rid of the impure lithium layer. The target is then brought in front of the evaporator for deposition. Three different experiments of 1 minute, 10 minutes and 60 minutes evaporation time were done. A partially masked silicon witness plate is used to find the thickness of lithium deposition for various evaporation times. The lithium thickness on the silicon witness plate is found using DEKTAK profilometer. Table 3 shows effective lithium thickness measured using a silicon witness plate for various lithium evaporation times.

<table>
<thead>
<tr>
<th>Lithium evaporation time (minutes)</th>
<th>Effective lithium thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.079±0.018</td>
</tr>
<tr>
<td>10</td>
<td>0.370±0.001</td>
</tr>
<tr>
<td>60</td>
<td>2.001±0.088</td>
</tr>
</tbody>
</table>

Table 3 - Effective lithium thickness for various lithium evaporation times

### 3.4 Step 4: Chemical sputtering experiments

A Hydrogen plasma environment is used in all the experiments to estimate the chemical erosion of the target. Three different experiments are conducted for different target positions with five different biasing conditions (0V, -500V, -1000V, -1500V and -2000V) and three different target temperatures (27°C, 100°C and 200°C)
as discussed below.

1. With the ATJ graphite side under the RF coil facing the sniffer tube to capture line of sight chemically sputtered species.

2. With the Li/ATJ graphite target under the RF coil facing the sniffer tube to study the effect of lithium treatments on chemical sputtering.

3. With the target in a faraway position from the sniffer tube to measure the baseline or wall contribution for getting more information on our wall conditions. This can be subtracted out if necessary to get the exact chemical sputtering contribution due to the target alone. Table 4 shows the list of main experiments conducted for this work.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Lithium evaporation time (minutes)</th>
<th>Biasing voltages (V)</th>
<th>Target temperature (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1: Plain ATJ and Li/ATJ</td>
<td>1</td>
<td>0,-500,-1000,-1500,-2000</td>
<td>27C,100C,200C</td>
</tr>
<tr>
<td>Experiment 2: Plain ATJ and Li/ATJ</td>
<td>10</td>
<td>0,-500,-1000,-1500,-2000</td>
<td>27C,100C,200C</td>
</tr>
<tr>
<td>Experiment 3: Plain ATJ and Li/ATJ</td>
<td>60</td>
<td>0,-500,-1000,-1500,-2000</td>
<td>27C,100C,200C</td>
</tr>
</tbody>
</table>

Table 4 - List of main experiments conducted

10W hydrogen RF plasma is ignited using a RF power supply. Usually for plasma based experiments like this, methane from chamber walls dominate the methane contribution from the actual target. Using a higher RF power increases the background wall contribution. Hence, a lower power is used to decrease the plasma
from spreading throughout the chamber, thereby reducing the chamber contribution.

The hydrogen plasma used in these experiments is a $T_e \approx 2\text{eV}$ laboratory plasma.

Biasing the target in addition to low power enables the plasma to be focused on to the target area. MSRGA is used to monitor the partial pressures of selected masses in 1–50 amu range in the remote sampling chamber. The MSRGA also allows us to monitor partial pressures of selected mass peaks versus exposure time (P vs T scans) which enables us to determine the steady conditions. The MSRGA scans are collected after initial transients (usually a couple minutes). Sometimes, small transients occur, due to moving the linear feed-through to various locations.

Multiple MSRGA scans are collected at each condition to determine the mean and standard deviation of partial pressures at specific masses which is then used for error propagation analysis. Duration of each MSRGA scan is about 1 minute. All the scans for various experiments are taken with the same duration to maintain the consistency of the experiments. Before the starting the experiments, the MSRGA is calibrated to the ion gauge pressure reading on the sampling chamber to main consistency, and also it was made sure that the chemical sputtering signals from both sides of the target were there same. If there is any residual lithium to begin with on one side, it will alter the measurements significantly. If the signals are not the same, a subtraction of the signals has to be done during the analysis. Hence proper care was taken to ensure the signal contribution were same on both sides. The IIAX chamber is baked before each experiment to get rid of the water vapor from the chamber walls.
3.5 Target heating

As discussed in earlier chapter, ATJ graphite target is heated by joule heating mechanism. Around 15A of current is passed through the target to induce heat in the target. The target temperature profile is given by the plot in Figure 20. The experimental temperature profile of the ATJ graphite can be fit by the equation

\[ y = 197.7 e^{-t/18.1} + 2.2 \]

The time constant is found to be ~18 minutes from the fit equation. It takes about 18 minutes for the temperature to drop to \( T_{\text{max}}/e \) which in our case ~74°C. The target cannot be kept hot during the experiments because the target is biased during experiments. Both heating and biasing cannot be done at the same time, because we may ruin the power supplies.
### 3.6 Data analysis and error propagation

Three distinct groups of masses are identified for these chemical sputtering experiments. They are:

1. Masses 12-16 that corresponds to methane (single carbon chain) family
2. Masses 25-30 that corresponds to ethane (double carbon chain) family and carbon monoxide (28).
3. Masses 37-44 that corresponds to propane (triple carbon chain) family and carbon dioxide (44).

---

**Figure 20 - Cooling profile of the ATJ graphite target**

![Experimental results](image)

<table>
<thead>
<tr>
<th>Model</th>
<th>ExpDec1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>$y = A_1 \exp(-x/t_1)$</td>
</tr>
<tr>
<td>Reduced Chi-Square</td>
<td>0</td>
</tr>
<tr>
<td>Adj. R-Square</td>
<td>--</td>
</tr>
</tbody>
</table>

| Mean | $y_0$ | 2.28736 | -- |
| Mean | $A_1$ | 197.71264 | -- |
| Mean | $t_1$ | 18.11449 | -- |
In the last two groups, masses 28 and 44 are dominant compared to the surrounding masses. Hence, major contribution for these groups comes from carbon oxide group. Therefore, the emission of hydrocarbons of length 2 and 3 is deemed negligible [48]. Hence, they will not be considered in our data analysis. Chemical sputtering products are determined by a matrix inversion approach. The RGA signals at specific masses from the lithiated ATJ case are subtracted from the ATJ case directly due to ability of our set-up as both have the same background contributions. Direct comparison helps in determining the relative suppression percentage from ATJ graphite to lithiated ATJ graphite. The partial pressures of the desired species for example, methane can be calculated from the following matrix equation.

\[ \mathbf{C}.p = s \]  \hspace{1cm} 3.2

C represents our cracking pattern matrix. S represents the partial pressures at specific masses and p is the partial pressures of the desired species. The specific partial pressure signals were multiplied with the inverse of the corresponding cracking pattern matrix to obtain the individual partial pressures of the desired chemical sputtering species which is methane in our case. Five linear equations are used in this analysis and they are as follows.

\[ S_{15} = 0.203 P_{CH_4} \]

\[ S_{16} = 0.203 P_{CH_4} + 0.230 P_{O_2} + 0.246 P_{CO_2} \]

\[ S_{18} = 0.006 P_{H_2O} \]

\[ S_{28} = 0.867 P_{N_2} + 0.092 P_{CO_2} \]

\[ S_{44} = 0.490 P_{CO_2} \]
3.6.1 Error analysis

There are two main types of error in these kinds of experiments are:

1. Absolute Error
2. Statistical Error

Absolute error occurs in taking a particular measurement in a system. For our experiments, the absolute error includes the systematic error of the RGA, error due to calibration and measurement of the system, error due to initial base line conditions of the chamber each time the experiments are done, error due to the purity of hydrogen gas used in the experiments, error due to moving the target for various target configurations, error due to evolution of the target structure over the course of experiments, error due to data acquisition time interval, and many more. Due to the complexity involved in determining these errors, they are neglected for this analysis, but incorporated into results by taking multiple data sets. Statistical error will be propagated for this analysis.

A statistical error is the amount by which an observation differs from its expected value. Statistical errors are relatively easy to analyze. A detailed statistical error analysis is done for our error propagation. Each experiment is repeated a number \( n \) of times, from which the measured values \( x_1, \ldots, x_n \) are obtained. Practical constraints of time and resources limit the number of acquisitions to \( n = 3 \) samples per type of experiment. As an appropriate estimator of the expected average value, we use the arithmetic mean

\[
\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i
\]

and since we assume a normal (Gaussian) distributed population
around the mean, we calculate the variance $\sigma^2$ as

$$\sigma^2 = \frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2$$

Since our statistical sample is limited to few acquisitions per experiment, we decide to compute the prediction interval by conservatively assuming an unknown-mean unknown-variance statistics, so that the interval results equal to

$$\bar{x} \pm \frac{t\sigma}{\sqrt{1 + \frac{1}{n}}}$$

where $t$ is the 100((1-p)/2) percentile at confidence $p$ of the t-Student distribution with $n-1$ degrees of freedom. The value of $t$ can be found tabulated or can be numerically evaluated from the inverse of the Student distribution,

$$t = F^{-1}(p/v)$$

where $v = n - 1$ and the student distribution $F$ is given by

$$p = F(t, v) = \int_{-\infty}^{t} \frac{1}{\sqrt{\pi v}} \Gamma \left( \frac{v}{2} \right) \Gamma \left( \frac{v+1}{2} \right) \left( 1 + \frac{z^2}{v} \right)^{-\frac{v+1}{2}} dz$$

and $\Gamma$ is the Gamma function. The values of $t$ for $n = 3$ are reported in Table 5 at several percentage of confidence.

<table>
<thead>
<tr>
<th>p[%]</th>
<th>$t$-Student</th>
</tr>
</thead>
<tbody>
<tr>
<td>85%</td>
<td>1.38621</td>
</tr>
<tr>
<td>90%</td>
<td>1.88562</td>
</tr>
<tr>
<td>95%</td>
<td>2.91998</td>
</tr>
<tr>
<td>99%</td>
<td>6.96456</td>
</tr>
</tbody>
</table>

Table 5 - Student parameter for n=3 (2 degrees of freedom) at several percentage of confidence.

During the analysis of our measurements we will assume 85% of confidence for all
error evaluations, so that the measure for each condition will be given within the following prediction interval

\[ \bar{x} \pm 1.2\sigma \] ..................................................3.13

The error in calculating the partial pressures of methane in our analysis is determined by classical McClintock formula. The uncertainty of quantity \( f \) with its dependent variables \( x_1, x_2, x_3... \) is described by the McClintock formula as

\[ \sigma_f = \sqrt{\left( \left( \frac{\partial f}{\partial x_1} \right)^2 \sigma^2 x_1 + \left( \frac{\partial f}{\partial x_2} \right)^2 \sigma^2 x_2 + \left( \frac{\partial f}{\partial x_3} \right)^2 \sigma^2 x_3 + \cdots \right)} \] ..................................................3.14

The equations leading to estimating the absolute error in calculating methane signal are given by

\[ S_{15} = a_{15} \cdot P_{CH_4} \] ..................................................3.15

\[ P_{CH_4} = \frac{S_{15}}{a_{15}} \] ..................................................3.16

\[ \Delta P_{CH_4} = \sqrt{\left( \frac{1}{a_{15}} \right)^2 (\Delta S_{15})^2 + \left( \frac{S_{15}}{a_{15}^2} \right)^2 (\Delta a_{15})^2} \] ....................3.17

\( S_{15} \) represents the mean value of signal at mass 15. \( P_{CH_4} \) is the partial pressure of methane, \( a_{15} \) is the mean cracking pattern ratio of methane at mass 15 which is obtained from the cracking pattern analysis, \( \Delta S_{15} \) represents the standard deviation in of signal at mass 15, \( \Delta a_{15} \) is the standard deviation of cracking pattern ratio of methane at mass 15. \( \Delta P_{CH_4} \) is the absolute error in calculating methane.

Signal at peak 15 is used in determining partial pressure of methane because of its high signal intensity at that mass which leads to the lowest error value. In addition, there is little to no interference at this mass. There is no NH (mass 15) in the system.
Chapter 4 : RESULTS AND DISCUSSION

4.1 System calibration

4.1.1 ATJ graphite target
Surface profilometry is done on the ATJ graphite target to know the surface roughness. For soft materials like graphite, surface roughness is highly dependent on the grit size of the sand paper that is used for cleaning after experiments. Smaller the grit size, smaller is the surface roughness and larger the grit size, larger is the surface roughness. A smaller grit size sand paper was used in cleaning the ATJ graphite after experiments to maintain consistency. The surface roughness of the ATJ graphite that is used in these experiments is found be 0.410±0.013µm using DEKTAK surface profilometer.

4.1.2 Chamber background/no target characterization
As it was discussed earlier, IIAX chamber is made out of stainless steel and pumped with oil-based mechanical pumps so the chamber itself is a huge source of carbon in our experiments. In order to understand the contribution from the chamber, the ATJ graphite target is removed from the chamber and chamber is subjected to 10W hydrogen plasma. Figure 21 is the MSRGA spectrum of the IIAX chamber without ATJ graphite target. It can be clearly observed that the methane signature peaks (12, 13, 14, 15 and 16) are not present when there is just hydrogen gas flow in the chamber. When the plasma is turned ON, the methane signature peaks show up. This experiment is very critical to understand the amount of background contribution that is inherently present in our experiments. This background contribution cannot be
eliminated but it could be subtracted to get the exact contribution due to ATJ graphite target, if necessary.

![Graph showing partial pressure versus mass (amu) for different conditions](image)

**Figure 21 - MSRGA spectrum of the IIAX chamber without ATJ graphite target**

### 4.1.3 ATJ graphite target characterization

In order to understand the contribution from the target, ATJ graphite alone was installed in the chamber without any traces of lithium in the ATJ graphite as well as the chamber. 10W plasma was ignited with the ATJ graphite target facing the sniffer.

Pressure versus time (trend) MSRGA spectrum gives the partial pressures of the desired mass as function of time. These types of plots help in understanding the time evolution of the signals. Figure 22 is the pressure vs. time MSRGA spectrum of ATJ target facing sniffer in hydrogen plasma. Methane signature peaks (particularly 15 and 16) show up when the plasma is turned on. It can also be observed that peaks 15 and 16 drop slowly and they are relatively flat over the period of time. Water vapor
cracks at peak 17 and 18. From the plots, it is clear that the peak 18 is higher than peaks 15 and 16. Water vapor is undesirable for these types of experiments as they increase the production of carbon dioxide and carbon monoxide than the actual chemical sputtering products. Higher water vapor content can make the evaporated lithium layer impure quickly. Hence, it is very important to eliminate water vapor from the ATJ graphite target before doing the experiments.

![Graph showing pressure vs. time spectrum of ATJ graphite target in 10W hydrogen plasma](image)

**Figure 22 -** Pressure vs. time spectrum of ATJ graphite target in 10W hydrogen plasma

### 4.1.4 Importance of baking

As discussed earlier, water vapor peaks dominate as ATJ graphite acts like sponge
and absorbs water vapor. When ATJ graphite is exposed to a plasma environment, water vapor comes out of it. Another better and efficient way to drive away water vapor from the target is to bake the target to high temperatures like 350C for 2-3 hours. Joule heating set-up was used to heat the target to high temperatures. The water vapor content in the IIAX chamber is also significant, hence the chamber is baked at 200C using an external heating tape to drive away the water vapor. Figure 23 is the MSRGA spectrum of the ATJ graphite target in 10W hydrogen plasma before baking and Figure 24 is the MSRGA spectrum of the ATJ graphite target in 10W hydrogen plasma after baking. It can be observed that before baking the ATJ graphite, the water vapor peak was dominating the spectrum, whereas after baking the target, methane signature peaks (particularly 15 and 16) were dominating the spectrum. Baking effects from two different target locations namely in front of sniffer tube and away from sniffer tube are captured for better understanding.

Figure 23 - MSRGA spectrum of the ATJ graphite target in 10W H₂ plasma before baking
4.1.5 Validation of signal origin from ATJ graphite target

As it was observed from the earlier plots that chamber contributes significantly to the chemical sputtering species, it is very important to make sure that the ATJ graphite is contributing to the chemical sputtering species recorded in the MSRGA. The surface area of the IIAX chamber is huge compared to the surface area of the ATJ graphite target hence this experiment is critical in determining the signal origin in the MSRGA. For this purpose, ATJ graphite target was heated to 200°C and allowed to cool at different locations from the sniffer tube. The ATJ target is initially situated at the sniffer and gradually moved away. Figure 25 is MSRGA spectrum of ATJ graphite target due to heating at different locations from the sniffer. It can be clearly observed that the methane related peaks decreases as we go away from the sniffer tube, clearly indicating target contribution. It can be observed from the relative intensities of the partial

---

**Figure 24** - MSRGA spectrum of the ATJ graphite target in 10W H₂ plasma after baking
pressures that the water vapor peak (18) stays the same while the methane peaks go down.

Figure 25 - MSRGA spectrum of ATJ graphite target at different locations from the sniffer

4.1.6 Methane trapping by ATJ graphite target

All the chemical sputtering experiments in this work is done starting with ATJ graphite target at 27C (room temperature) and gradually increasing the target temperature to 200C. In order to understand if doing the experiments in a sequence of 27C, 100C and 200C (Sequence 1) gives the same results as doing the experiments in the order of 200C, 100C and 27 (Sequence 2), chemical sputtering measurements of ATJ graphite is done in both sequences. Figure 26 is a plot of methane partial pressure vs. temperature taken in both the sequence. It can be observed that the methane production at 27C in sequence 1 is almost 53±6% higher than 27C experiments in sequence 2. Also methane production at 100C in sequence 1
is 17±2% higher than 100C experiments in sequence 2. The possible explanation for this type of behavior could be that ATJ graphite acts like a sponge and traps methane from previous experiments. As the ATJ graphite is heated, it starts to drive away methane resulting in lower methane production in sequence 2.

![Diagram](image)

Figure 26 - Methane production from ATJ graphite target as a function of heating and cooling

4.1.7 Lithium calibration

a. Lithium foil experiments: A 0.03” thick, 0.75” wide lithium foil was attached to one side of the ATJ graphite to understand the behavior of full lithium coverage. The Lithium foil is exposed to 10W hydrogen plasma at 27C (room temperature). Pressure vs. time MSRGA scans were collected with lithium foil facing sniffer. It can be clearly observed from Figure 27, that methane signature peaks gradually goes down due to automatic glow discharge of the lithium surface. Ideally, we expect only the wall contribution as the lithium is completely covering the ATJ graphite surface.
But we see considerable methane signature peaks (15 and 16). To begin with, lithium reacts with the water vapor in the chamber forming impurity layer quickly on the top surface of the lithium layer. The thickness of the impurity layer depends on the value of the background pressure and composition of the gases present in the background pressure on particular day. In our case, we see methane peaks because lithium absorbs some of the methane that was re-deposited during the hydrogen plasma discharge. Yagi et al. [37] reports that in order to obtain a full effect of lithium intercalation, preconditioning of lithium surface is necessary as it suppresses chemical erosion of graphite. From Figure 5 in Chapter 1, it can be observed from Yagi’s work that methane yield was more in the case of lithium deposited surfaces rather than lithium free surfaces. As the lithium deposited surfaces were subjected to glow discharge conditioning, the methane peaks completely disappeared. Yagi hypothesizes that hydrogen glow discharge conditioning removes oxygen impurities from graphite surface. Hence, the intercalated lithium diffuses towards the top surface exposing fresh lithium to the plasma. The result of glow discharge conditioning effect can be observed from Figure 27. Initially the methane related peaks were high but they gradually start to decrease as time progresses due to automatic glow discharge conditioning of the lithium surface. It can also be observed that water vapor peak (18) goes down and this is also attributed to glow discharge cleaning which helps to drive away water vapor from the lithium surface. Figure 28 is the comparison of all three ATJ graphite target positions in 10W hydrogen plasma after one hour glow discharge conditioning. It can be observed that the methane
production from the lithium foil is tending to reach steady state. Methane peaks of lithium foil are higher than ATJ graphite and this is due to re-deposition of methane from walls on the lithium foil surface. Partial pressure values of methane related peaks (15 and 16) of the lithium foil side would slowly drop below the partial pressure values of methane related peaks of the ATJ graphite if it is subjected to longer glow discharge conditioning. Methane related peaks of the ATJ side and lithium foil side is higher than the wall case, where the target set-up is moved away to the chamber walls. This also reinforces the contribution from target. Cleaning time of the lithium surfaces depends on the thickness of the impurity layer which is hard to determine. The thickness of the impurity in turn depends on the background pressure, lithium deposition time, graphite temperature, etc.

![Lithium foil facing sniffer with plasma ON](image)

Figure 27 - Time evolution spectrum of lithium foil facing the sniffer in 10W hydrogen plasma
b. Lithium target experiments:

To have a better understanding of behavior of lithium surfaces, a rectangular lithium chunk of 2.5”X1.5”X0.5” was used in the place of ATJ target. The rectangular lithium chunk was exposed to 10W hydrogen plasma. Time evolution MSRGA spectrum of the lithium chunk facing the sniffer tube is recorded. It can be observed from Figure 29 that methane related peaks go down gradually due to automatic glow discharge conditioning clearly, indicating the importance of glow discharge conditioning to see a reasonable chemical sputtering suppression. Figure 30 is the overlay spectrum of lithium chunk at the center facing the sniffer tube and away from the sniffer to the walls. It can be observed that the methane signature peaks
increases when the lithium chunk is facing the sniffer due to re-deposited methane from the walls. The magnitude of methane peak is reduced when the lithium chunk is pulled to the chamber walls indicating the wall contribution.

Figure 29 - Zoom in view of time evolution spectrum of rectangular lithium chunk facing the sniffer in 10W hydrogen plasma

Figure 30 - Overlay spectrum of lithium chunk at the center facing the sniffer tube and away from the sniffer to the walls
A couple of more experiments were done with the rectangular lithium chunk. In the first experiment, the rectangular face of the lithium chunk was at the center facing the RF coil horizontally but was not line of sight to the sniffer tube. It can be observed from Figure 31 that the methane related peaks reach steady state quickly and stay reasonably constant over the period of time. Since the lithium chunk was not line of sight to the sniffer tube, this case is like the wall alone case. This plot coincides with wall case where peaks reach steady state quickly compared to lithium cases.

In the second experiment, the rectangular face of the lithium chunk was at the center facing sniffer tube i.e. it was line of sight to the sniffer tube. It can be observed from Figure 32 that methane related peaks gradually drop down as time progresses due to glow discharge conditioning of the lithium surface. The methane partial pressure in the first experiment is much higher than the methane partial pressure in the second experiment. This is because the first experiment was done before the second experiment. The lithium surface was cleaned due to glow discharge conditioning from the first experiment so the methane partial pressure was less compared to the first experiment to even begin with.
Figure 31 - Time evolution spectrum from rectangular face of the lithium chunk at the center facing the RF coil horizontally

Figure 32 - Time evolution spectrum from rectangular face of the lithium chunk at the center facing the sniffer tube horizontally
4.2 Chemical sputtering suppression due to lithium application

Chemical sputtering measurements are taken for three different target temperatures (27°C, 100°C and 200°C) and five different biasing voltages (0, -500V, -1000V, -1500V and -2000V). The experimental procedure is described in Chapter 3. The results are summarized for different target temperatures. In the results, methane partial pressure from ATJ graphite target and lithiated ATJ graphite is plotted for different lithium thickness. Not all biasing condition data are included because the statistical scattering was huge in that data set.

a. 27°C:

It can be observed from Figure 33, that even at room temperature (27°C), chemical sputtering suppression due to lithium application is pronounced. Chemical sputtering suppression strongly depends on the amount of lithium deposited on the ATJ graphite surface. More the lithium evaporated, higher the chemical sputtering suppression effect. We also observe that when the biasing voltage is increased, methane production is also increased. This is due to physical induced chemical sputtering.
b.100°C:

From Figure 34, lithium suppression effect can be observed for 100°C target temperature. The lithium chemical suppression effect is function of lithium thickness on the ATJ graphite surface.
c. 200°C:

It can be observed from Figures 35, that lithium sputtering effect can be observed more clearly at 200°C ATJ graphite target temperature. There is a noticeable increase in chemical sputtering suppression as the lithium thickness is increased. Figure 36 shows the lithium suppression effect for different target temperatures at a bias voltage of -1000V. Methane trapping effect can be observed as discussed earlier. Table 6 is summary of quantitative methane suppression percentages due to lithium application on ATJ graphite for different lithium evaporation times.
Figure 35 - Methane partial pressure vs. Lithium evaporation time for ATJ graphite target temperature of 200C and no bias voltage

Figure 36 - Methane partial pressure vs. Lithium evaporation time for ATJ graphite target temperature of 200C and no bias voltage
<table>
<thead>
<tr>
<th>Target Temperature (°C)</th>
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<th>Lithium thickness (µm)</th>
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Table 6 - Suppression percentages of methane production due to lithium application on ATJ graphite, for different lithium deposition times.

It can be observed from the results that the thicker the lithium layer, the larger the chemical sputtering effect. The amount of lithium deposited on ATJ graphite is a linear function of the lithium evaporation time. The surface roughness of the ATJ
graphite target was found to be 0.410±0.013µm. In case of 60 minutes lithium evaporation, the lithium layer thickness is 2.001±0.088µm which is more than the surface roughness of the ATJ graphite. Hence we find greater suppression at 60 minutes lithium evaporation for all the data. Typically more suppression effect will be expected at 60 minutes lithium evaporation as it covers the lithium completely but we know that lithium intercalates onto ATJ graphite so it is hard to say if the lithium would have completely covered the ATJ graphite surface or not. To summarize, when the thickness of the deposited layer is greater than the surface roughness of the ATJ graphite layer, we observe greater chemical sputtering suppression. The data show a clear and consistent trend of chemical sputtering suppression percentages versus lithium thickness. Finally it can be hypothesized that fresh lithium surface and thickness of lithium layer greater the surface roughness of the ATJ graphite layer are vital to chemical sputtering suppression effect. Lithium application suppresses the chemical sputtering of ATJ graphite. A possible reason for suppression could be that the hydrogen glow discharge inserts hydrogen atoms on the lithium surface. The hydrogen atoms interact with lithium atoms to Li-H or Li-O-H complex which protect the underlying later from chemically interacting with the hydrogen plasma.
Chapter 5 : CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

Chemical sputtering measurements of plain and lithiated ATJ graphite in hydrogen plasma have been conducted in the IIAX (Ion-surface InterAction eXperiment) facility to understand the suppression effects of lithium coatings on ATJ graphite. It can be concluded from this work that lithium deposition on ATJ graphite shows the suppression of chemical sputtering products, especially methane. The larger the thickness of lithium layer, the higher the percentage of chemical sputtering suppression. The ability to rotate the target in front of the “sniffer” tube from a bare graphite side to a lithium-coated graphite side allows direct comparison with the background signal in this set-up. In-situ lithium evaporation, a RF plasma source, MSRGA and a bias-able/heatable target are necessary experimental components of this work. A simple mathematical approach that includes only single-carbon hydrocarbons is presented in this work. The species that were included in the analysis of this work are CH$_4$, H$_2$O, N$_2$, O$_2$ and CO$_2$. The chemical erosion studies conducted in a plasma chamber like this, as opposed to beam experiments, provide a better understanding of the phenomenon taking place in tokamaks. Previous work on chemical sputtering of graphite was done either using ion beam or plasma under steady state conditions, but in machines like NSTX, plasma shots last for 1-2 seconds so it is very important to understand the transient behavior rather the steady state behavior. This chemical sputtering suppression work was done in the transient...
regime, making it more relevant to NSTX-like machines. To conclude, a fresh lithium surface and lithium thickness greater than the surface roughness of ATJ graphite is the key to chemical sputtering suppression.

For NSTX like machines that uses graphite, this work proves that lithium application significantly reduces the chemical sputtering of graphite, and the thickness of the lithium coating on the graphite plays a critical role in determining the extent of chemical sputtering suppression.

5.2 Future work

A much larger ATJ graphite target can be used to increase the target contribution significantly. Helium glow discharge cleaning of ATJ graphite target surface can be done to remove the oxygen and hydrogen from surface. Argon plasma cleaning of the deposited lithium coating can be done to remove the top few impurity layers and expose fresh lithium to the hydrogen plasma. For the lithium coated experiments, the lithium can be coated on all the surfaces rather than one particular face. Uniform lithium coating can be achieved by improving the evaporator set-up. A separate load lock chamber can be installed for doing lithium evaporation and wall case experiments. A ceramic target heater set-up can be installed to maintain the target at a desired temperature during experiments so that the target can be biased simultaneously. This will help to heat and bias the target in plasma during the experiments.

Future work on IIAX will focus on studying deuterium uptake of lithium on molybdenum and boronized molybdenum. Physical sputtering measurements of
lithium on mixed materials (Li/TZM, Li/Mo, Li/B/Mo) and ionization fraction measurements of the sputtered lithium in IIAX will be an interesting topic, as NSTX has plans to use TZM in their machine. XPS (X-ray photoelectron spectroscopy) can be installed in the IIAX to study the lithium surface interaction on different materials in detail.
References


[25] Majeski, R. et al. The impact of lithium wall coatings on NSTX discharges and


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