Temperature dependence of liquid lithium film formation and deuterium retention on hot W samples studied by LID-QMS. Implications for future fusion reactors

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Abstract

Liquid metal (LM) divertor concepts explore an alternative solution to the challenging power/particle exhaust issues in future magnetic fusion reactors. Among them, lithium (Li) is the most promising material. Its use has shown important advantages in terms of improved H-mode plasma confinement and heat handling capabilities. In such scenario, a possible combination of tungsten (W) on the first wall and liquid Li on the divertor could be an acceptable solution, but several issues related to material compatibility remain open. In particular, the co-deposition of Li and hydrogen isotopes on W components could increase the associated tritium retention and represent a safety risk, especially if these co-deposits can uncontrollably grow in remote/plasma shadowed zones of the first wall. In this work, the retention of Li and deuterium (D) on tungsten at different surface temperature (200 °C–400 °C) has been studied by exposing W samples to Li evaporation under several D₂ gaseous environments. Deuterium retention in the W–Li films has been quantified by using laser induced desorption-mass spectrometry (LID-QMS). Additional techniques as thermal desorption spectroscopy, secondary ion mass spectrometry, profilometry and flame atomic emission spectroscopy were implemented to corroborate the retention results and for the qualitative and quantitative characterization of the films. The results showed a negligible (below LID sensibility) D uptake at T_{surface} = 225 °C, when the W–Li layer is exposed to simultaneous Li evaporation and D₂ gas exposition (0.67 Pa). Pre-lithiated samples were also exposed to higher D₂ pressures (133.3 Pa) at different temperatures (200 °C–400 °C). A non-linear drastic reduction in the D retention with increasing temperatures was found on the W–Li films, presenting a D/Li atomic ratio at 400 °C lower than 0.1 at.% on a thin film of ≈100 nm thick. These results bode well (in terms of tritium inventory) for the potential utilization of this material combination in a real reactor scenario.

Keywords: co-deposition, deuterium retention, tungsten, lithium, fusion reactors, LID

(Some figures may appear in colour only in the online journal)
1. Introduction

The research in the field of plasma facing materials (PFMs) is decisive for the development of magnetic nuclear fusion energy and the economic viability of commercial reactors. At present, after decades of intense investigation, tungsten (W) has become the main candidate to be used in future reactors and it has been selected to be used in the ITER divertor [1, 2]. Among the main problems related with the surrounding materials exposed to burning D–T plasma during the operation of a future reactor, the hydrogen isotope retention (tritium inventory) and the power exhaust handling are among the most challenging issues to be solved for the successful development of fusion energy. In ITER during short pulsed operation, the acceptable nominal power load in the divertor region must be limited to 10 MW m$^{-2}$ while transient events as edge localized modes (ELMs), disruptions, runaways and other uncontrolled events can increase the heat loads up to 1 GW m$^{-2}$ [3]. Moreover, it is evident that the longer pulsed mode operation and the associated neutron fluxes will affect to the power handling and associated PFM damage in a reactor prototype as DEMO, thus making the removal of power exhaust and the concomitant PFMs degradation even more demanding.

Liquid metal (LM) components (in particular lithium, Li) offer an innovative solution to this issue as its surface is, in principle, free of irreversible damage. The use of Li in several magnetic devices has shown unique advantages in terms of plasma confinement improvement (at wall temperatures much lower compared to the proposed in the following sections of this paper for a first wall low hydrogenic retention DEMO scenario) and heat handling capabilities [4–6], becoming an option that is currently studied in alternative divertor concepts [7]. Despite these positive effects, the main drawback associated with the use of liquid lithium is probably its strong affinity with hydrogen isotopes as a result of its alkaline and very reactive nature. As the total moveable tritium inventory for the in vessel components is limited to 700 g [8], the potential tritium uptake of Li PFM could suppose a serious risk for D–T operation.

Considering a DEMO scenario combining a conservative solid (hot) tungsten first wall and a liquid Li element at the divertor, where the power exhaust is concentrated and mitigated, as viable in terms of technology and engineering development, the fuel retention problem on the divertor could be solved by periodic baking at $T \leq 550$ °C [5] or ultimately, with recirculating closed loop solutions [9–11]. These ideas propose the recirculation of liquid lithium present in the PFCs out of the vessel to be re-injected in the divertor components after its regeneration (with the total desorption of the hydrogen isotopes from Li elements at moderate temperatures [12–16]). Notwithstanding, for the development of these alternative solutions, other issues related with this material compatibility in terms of material migration and mixing (among others) must be investigated. Unavoidably, in a future reactor the continuous plasma bombardment onto the PFM will produce its sputtering. With this W–Li PFM considered scenario, the creation of mixed W–Li films, with deposition of W on Li and vice versa will take place. Moreover, the effects of the associated neutron flux (that is expected to create defects and traps in the materials, increasing in this way the associated fuel retention) in these processes needs to be taken into account for the global integration of this PFM solution in a reactor. All these issues, however, are out of the scope of this paper.

Concerning tritium inventory build-up, the presence of liquid lithium on the divertor will produce evaporative Li fluxes and a concomitant thermal co-deposition of Li atoms on W surfaces that will be associated with an increase in the fuel retention on such films. In the last years, intense experimental and modelling work has addressed the surface temperature influence on the behaviour/stability of Li–D containing films deposited in different substrates as well as several issues that would be associated with the possible integration of this PFM solution in a reactor environment. Thus for example, the results of a surface analysis study on nickel [17] substrates, on which LiH films were created, indicated unstable hydride (LiH) films when the surface temperature was increased up to 340 °C. This behaviour was found in ultrathin (0.5–10 monolayer (ML), thickness $\ll$3 nm) LiH films. Additionally, Capece et al [18] also studied the temperature effect on the D retention in ultrathin lithium films deposited on molybdenum (TzM) alloy confirming the decomposition of lithium deuteride at temperatures below 400 °C. Another important related aspect is the material erosion by sputtering of liquid Li–D containing films. This issue was firstly studied by Allain et al [19] being also investigated in the NSTX device [20] on liquid lithium deposited on graphite and molybdenum substrates. They found increasing sputtering yields for higher temperatures in Li–D and Li–Li self-sputtering [21]. In NSTX [20] an enhancement (factor 2) in the Li sputtering was found at temperatures between 400 °C–500 °C compared to 200 °C. Moreover, preferential sputtering of the D atoms present in Li–D containing films was found [22]. These results would imply a reduction of the Li film thickness deposited on W and especially in the fuel retention in such films during the reactor operation, but it would lead to an increase in the input flux of Li impurities to the burning plasma. However, for the global evaluation of the plasma contamination by Li impurity at $T_{\text{Li,th}} > 400$ °C, evaporative fluxes rather than sputtering will dominate [16, 23]. Due to the exponential increase of the vapour pressure with temperature and the associated increase in the plasma contamination, conservative estimates have establish the upper limit for the temperature of the liquid lithium surfaces to values around 450 °C [23] in order to maintain a suitable plasma core confinement, thus avoiding its excessive dilution by Li impurities and the associated quenching of the D–T reactions. However, the utilization of temperature limits higher than 450 °C for the liquid Li surfaces could be possible as different works [24–26] have shown that even a lithium ion concentration higher than 10% in the plasma core (concentration that would be associated to $T_{\text{surface}}^{\text{Li}} > 450$ °C [26]) would be still compatible with the necessary confinement for the maintenance of the D–T burning plasma conditions.

The scope of this paper is the study of the thermal deposition of lithium and molecular D$_2$ on tungsten, trying to
analyze the potential problem derived from an uncontrolled growth of thick Li co-deposits in remote parts and/or plasma shadowed zones of the W first wall. On these parts this issue could be especially problematic due to the impossibility of direct cleaning by the plasma itself and/or auxiliary discharges without the replacement of the involved elements. Laser induced desorption (LID) assisted by mass spectrometry (QMS) was used to remove and quantify the deuterium uptake on W–Li–D containing films after the deposition of Li and deuterium (D) on tungsten, emphasizing on the dependency of the surface temperature on the net deuterium retention in such films.

The paper is structured as follows. Section 2 introduces the experimental setups and the work devoted to produce the W–Li–D samples, their laser irradiation and post mortem analyses. The experimental results (LID, TDS, SIMS, profilometry and FAES) are described in section 3. Section 4 discusses the experimental findings, relating them with the thermodynamic aspects of the thermal dependence of the deuterium absorption on the W–Li films as well as the possible implications of the obtained results in the potential application of the proposed PFM solution in a reactor scenario. Finally, section 5 summarizes the main conclusions obtained from this extensive experimental work.

2. Installations, procedures and techniques utilized during the experimentation

The experimental works performed during these studies can be divided into three separated phases:

1. Preparation of the W–Li–D samples by means of its deposition under different Li–D2 environments.
2. LID measurements after transportation of the samples in closed manipulators over-pressurized with dry argon to avoid atmospheric contamination.
3. Application of post mortem techniques for the total characterization of the W–Li–D films.

2.1. Preparation of W–Li–D samples

The deposition of lithium and deuterium on tungsten (cold rolled and high purity) rectangular (20.4 mm length, 17.5 mm width and 0.1 mm thick with an exposed area of 3.6 cm² and total mass, \( m = 0.72 \pm 0.04 \) g) samples was carried out in a stainless steel vacuum vessel (deposition chamber illustrated in figure 1) with an approximated volume of 5 l, pumped out by means of a turbomolecular pump in serial connection with a rough pump. Two different kind of Li–D2 interaction environments were used to prepare the samples:

- Simultaneous exposure to evaporative Li and gaseous D2 (co-deposition regime) under a D2 atmosphere \( p_{D2,\text{chamber}} = 0.67 \) Pa.
- Sequential exposure to Li and gaseous D2. Firstly, lithium was pre-deposited on W before exposing the created film to D2 at a higher pressure conditions \((\approx 133) \) Pa. Three different samples were prepared by changing the surface temperature (200 °C, 300 °C and 400 °C) during the Li and D2 exposure.

2.1.1. Simultaneous deposition of deuterium and lithium on W. One sample (named as wlid) was prepared by evaporating lithium in a molecular D2 \((0.67 \) Pa) environment while the sample temperature was maintained around 200–225 °C. This procedure, which could be denominated as thermal co-deposition, tried to simulate the molecular pressure levels existent on remote or plasma shadowed areas of a fusion reactor first wall during D–T operation.

Inside the deposition chamber a stainless steel oven (2.5 cm of diameter and 4 cm of height) filled with 2 grams of lithium was placed. The Li atoms were effused through a circular hole \((d = 1 \) cm) situated on the top of the oven. This device acted as a Knudsen cell for the Li atoms during the sample preparation procedure. The oven was heated up by using an electric resistance rolled around it. The lithium temperature during the process was measured with a type K thermocouple inserted in the Li bulk. A good equivalence between the measured temperature and the Li one was registered as the melting of the Li was visualized, with its corresponding temperature plateau, at 178 °C in the thermocouple, while \( T_{\text{melting}} = 180.5 °C \).

The tungsten samples were washed out in an ultrasound bath followed by baking \((150 °C)\) and finally cleaned with acetone and ethanol to eliminate dust and impurities. After this sample conditioning protocol, that is common for all the samples considered in this study, they were placed in a 30 cm length manipulator installed in the deposition chamber coupled with a gate valve. The sample was positioned at a distance of 26.5 mm, perpendicularly oriented to the oven effusion hole (see figure 2), forming its edges angles of \( \varphi_1 = 12° \) and \( \varphi_2 = 35° \) respect the normal direction to the effusion source. In this way, the sample encompasses an approximate solid angle \( (\omega) \) of around 0.63 sr respect the evaporation semispherical surface of the oven hole. As a consequence of the proximity of the sample during the oven heating for the Li evaporation, the radiation increases the sample temperature up to 200–225 °C. The temperature on the tungsten surface was measured using an infrared pyrometer \((150–1000 °C)\) measurement range). An ionization gauge (Bayard Alpert) was used to monitor de vacuum level inside the vessel (residual pressure around \( 10^{-5} \) Pa). Before starting the co-deposition, the sample was heated up to 550 °C during 30 min to degas residual water and hydrogen. The heating was performed with a W resistive filament, fed with a DC power supply, placed by means of other manipulator behind the sample holder very close but detached from it. The lithium bulk and oven were also outgassed (up to 300–325 °C) during 30 min. This general description and outgassing procedures were applied in the preparation of all the samples considered in this study.

After this procedure, the lithium present inside the oven is heated up to 450 °C. When it reaches this value, the deuterium gas is introduced in the chamber through a leak valve up to a total pressure of 0.67 Pa (capacitance manometer measurement) during 30 min in a continuous flow regime.
The temperature of the sample was monitored with the pyrometer, oscillating between 200–225 °C during all the exposure. A simple calculation of the evaporative flux of Li atoms gives a total number of evaporated lithium atoms in the oven around $4.3 \cdot 10^{20}$ during the whole oven heating procedure. Taking into account the angular position of the sample and the solid angle the total number of reaching Li atoms to the sample is estimated around $1.5 \cdot 10^{19}$ that roughly implies an average lithium film thickness of ~1 µm.

After this Li–D$_2$ exposure, the sample is prepared for the LID analysis. The manipulator is retracted, the whole chamber is vented with Argon and the manipulator gate valve is closed in over-pressure conditions. Then, the manipulator is transported from the deposition chamber to the LID chamber avoiding in this way, an atmospheric sample contamination that can affect to the Li–D films [27–29].

2.1.2. Pre-deposition of lithium on tungsten followed by high pressure D$_2$ gas exposition. In this case, pre-lithiation of the tungsten samples was performed by evaporating Li at 450 °C from the oven during 30 min in vacuum conditions (surface temperature around 200–225 °C on sample). After the pre-lithiation, the sample is exposed to a higher D$_2$ pressure environment (133 Pa) for 1 h. At the beginning of the D$_2$ exposure, the gate valve that connects the turbopump with the deposition chamber is closed to maintain this deuterium pressure without external puffing in static conditions (no pumping). It is important to note that the deuterium exposition must be started when the temperature of the lithium present in the oven is below its melting point to avoid its exposure to deuterium in liquid state. Previous trials showed that if deuterium is injected in the deposition chamber immediately after the deposition of lithium on the sample when it is still hot and liquid inside the oven, the liquid surface and bulk, that contains several grams, act as a sink for the D$_2$ molecules, avoiding the interaction of deuterium with the W–Li layer of the sample. In our experiments the exposure of the pre-lithiated samples to deuterium was carried out with temperatures lower than 100 °C inside the oven in all instances. However for the case of the simultaneous exposition with D$_2$ and Li (sample named as wlid, whose preparation was explained in the previous section), the exposure regime was a continuous gas injection, determining a D$_2$ pressure in the chamber of 0.67 Pa,
with continuous pumping. With this regime, it was possible to maintain the \( D_2 \) pressure level (0.67 Pa) with a lithium temperature of 450 °C in the oven, thus allowing the simultaneous exposure to Li and \( D_2 \) on the W sample.

This necessary cooling time of around 90 min for the pre-lithiated samples would unavoidably imply a contamination (oxidation) due to the interaction with residual gaseous molecules associated to the vacuum levels. Such levels (~10⁻³ Pa) can involve, considering that the total residual vacuum is exclusively water as extremely worst case approximation, an oxygenic impurity growth rate (as we do not have a proper in situ analysis, we generally consider them as LiO) on the sample surface of ~0.5 ML min⁻¹ [30]. Hence, the cooling time would produce a total amount of \( 10^{17} \) impurity particles present on sample surface (assuming 1 ML = 6·10¹⁴ particles cm⁻² [31]) and \( A_{\text{sample}} = 3.6 \text{cm}² \). Even in this extreme case, the impurity amount would be small compared to the remaining Li after the exposure to \( D_2 \) on samples as the FAES analyses gave a minimum lithium content on samples around \( 10^{18} \) atoms, for the case of the sample wld8 (see table 5). This experimental contamination of the Li films can produce a higher retention as has been experimentally and theoretically demonstrated in lithium-conditioned carbon walls [32]. However, our pre-lithiated samples did not contain any carbon content and the expected impurity deposition prior the \( D_2 \) exposure resulted much lower. As will be shown in section 3.2.2, the SIMS analyses showed a very low content of such lithium impurities compared to the pure lithium content. Hence, in principle, the major part of this retention can be considered due to the pure lithium films. Consequently, the unavoidable lithium impurity presence on samples may play a certain role in the retention, probably increasing it, but their effect in the global results can be considered small. Three different surfaces under high vacuum conditions. In our case the desorbed molecules associated to the vacuum levels. In such situation, the propagation of the pulsed heat flux is expected to be more pronounced. Consequently, taking into account all these particularities, for analysing the global thermal transfer in the \( z \) direction, to use an average value, between \( W \) and Li, for the reflectance, as well as for the thermo-physical values as diffusivity, etc., seems much more reasonable than use the normal values for solid lithium. The rest of the thermal characteristics for tungsten [37], lithium [38] and mean values between both

### Table 1. Physical and optical properties for W, Li and average values.

| Element            | \( c_p \) (J (Kg K)⁻¹) | \( \rho \) (Kg m⁻³) | \( k \) (W m⁻¹ K⁻¹) | \( D_3 \) (m² s⁻¹) | Reflectance |
|--------------------|------------------------|---------------------|---------------------|------------------|-------------|
| Tungsten (W)       | 130                    | 19 250              | 170                 | \( 6.79 \times 10^{-4} \) | 0.602       |
| Lithium (Li)       | 3750                   | 535                 | 85                  | \( 4.24 \times 10^{-4} \) | 0.941       |
| W–Li (av. value)   | 1940                   | 9918                | 128                 | \( 5.51 \times 10^{-5} \) | 0.772       |

2.2. Irradiation of W–Li–D samples with the Nd:YAG laser beam

Among laser methods [33], LID enables the in situ fuel removal and the measurement of the retained hydrogen isotopes under high vacuum conditions. In our case the desorbed hydrogen is detected and measured with a SRS 100 residual gas analyzer (RGA). For the irradiation of the samples a solid state (Nd:YAG) laser (LITRON LPY 600) operating in the first harmonic (1064 nm) and long pulse mode \( (\tau = 0.25 \text{ms}) \) has been used [34]. The average output of energy per pulse was 1067 ± 47 mJ. Measurements of beam energy were carried out by means of a pyroelectric joule meter. The original spot size of the laser was measured (sensitivity of 0.2 mm), presenting an approximate Gaussian distribution (close to top hat profile) with a full width half maximum value (FWHM) of 6.5 mm, corresponding to energy power density values of 3.3 J cm⁻² and 13 kW cm⁻². After focusing the laser with a converging lens \( (f = 400 \text{mm}) \), a beam diameter of 1.25 mm is obtained (see section 3.2.3). Consequently, the energetic characteristic of the laser were increased up to 90 J cm⁻² and 360 kW cm⁻². In all the analyses a frequency of 1 Hz was used. In order to estimate roughly the absorbed laser power, the energy losses due to reflection in the W–Li surfaces need to be taken into account. The reflectance \( (R) \) of W and Li exposed to infrared light (1064 nm) can be found in [35], being 0.60 the global value for tungsten and 0.94 for solid lithium. As will be explained later in the profilometry sections, the homogeneity of the deposition process produced an irregular surface, as the profilometry measurements demonstrated, showing zones with Li shortage with almost unique presence of W on surface. This deposition morphology existed before applying the laser shots. Moreover, the lithium film thickness constituted only a few microns that compared to the total thickness of the W substrate \( (100 \mu\text{m}) \) represents a very small fraction. Additionally, lithium melting was produced during the laser pulse and for liquid lithium the reflectance decreases, giving values of 0.7 at \( T_{\text{melting}}^\text{Li} \) and 0.6 at \( 2 T_{\text{melting}}^\text{Li} \) [36]. In such situation, the propagation of the pulsed heat flux is expected to be more pronounced. Consequently, taking into account all these particularities, for analysing the global thermal transfer in the \( z \) direction, to use an average value, between \( W \) and Li, for the reflectance, as well as for the thermo-physical values as diffusivity, etc., seems much more reasonable than use the normal values for solid lithium. The rest of the thermal characteristics for tungsten [37], lithium [38] and mean values between both

2.1.3. Preparation of a tungsten blank sample. Finally a blank tungsten sample (wld12) was prepared in order to compare the deuterium retention values of the W–Li films with the uptake of the lithium-free tungsten surface. After its outgassing, it was exposed to a \( D_2 \) gaseous environment \( (p = 133 \text{ Pa during 1 h}) \).

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| Element   | \( c_p \) (J (Kg K)⁻¹) | \( \rho \) (Kg m⁻³) | \( k \) (W m⁻¹ K⁻¹) | \( D_3 \) (m² s⁻¹) | Reflectance |
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| W–Li (av. value) | 1940                 | 9918                | 128                 | \( 5.51 \times 10^{-5} \) | 0.772       |

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elements, are presented together with the reflectance values in table 1.

The amount of hydrogen isotope desorbed from the hot spot will depend on the maximum temperature achieved on the surface during laser irradiation. This pulsed temperature change can be modeled by following the Fourier’s law of heat conduction. Assuming several simplifications [39], the solution of the 1D differential heat equation [40] gives the evolution of the temperature ($T$) at a depth $z$ and time lower or equal to the laser pulse length ($\tau$):

$$T(z, t \leq \tau) = T_0 + \frac{2I_0(1 - R)}{k} \cdot \sqrt{Dt} \cdot \text{ierfc} \left( \frac{z}{2\sqrt{Dt}} \right). \quad (1)$$

In this expression, ierfc is the integral of the complementary error function that can be evaluated in terms of the error function, $R$ is the reflectance for the irradiated surface, $k$ is the thermal conductivity and $D$ represents the thermal diffusivity. For a time greater than the pulse duration the temperature profile can be evaluated introducing another term delayed in a time factor ($t - \tau$) [40]. Applying this equation, computer simulations were performed in order to evaluate the temperature changes induced on the samples.

The simulations showed maximum temperatures between 900 °C–600 °C depending on the $z$ position. Even for the deepest point (100 µm) situated at the farthest distance from the laser beam incidence, the temperature rose up to 600 °C. Several experimental results have shown that the hydrogenic desorption from lithium is completed at these temperatures [12–14]. Consequently, these calculations indicated that the laser shot would be able to heat the sample and induce the total hydrogenic desorption. In any case, more diagnostics and post mortem analysis were performed to assure the complete removal of the hydrogenic content.

Once the samples are prepared and transported without atmospheric contamination to the LID facility, the manipulator is connected to the LID chamber whose elements are listed in figure 3. An intermediate small port connects the manipulator valve with the main valve of the LID chamber. This port is assembled to a mobile pumping unit before opening the manipulator valve, avoiding in this way the contact of the sample with air. Before introducing the sample in the LID chamber, it is necessary to pre-pump the manipulator (during 2–3h) with the mobile pumping unit to adequate its pressure to the very high vacuum conditions of the LID chamber ($\approx 0.8–1 \times 10^{-5}$ Pa). After introducing the sample in the LID chamber, the whole setup is pumped out for ~12 h to reach the existing previous vacuum level before connecting the manipulator. This procedure allows assuring optimal vacuum levels inside the LID chamber, that are necessary for a good analysis avoiding in this way the increase in the residual contents of deuterium, hydrogen, HD and water inside the chamber. In principle, the interaction of the Li–D containing films with the residual vacuum during this pumping period would be able to produce the formation of impurities as was previously commented in section 2.1.2. Taking into account the same reasoning, the longer exposure time could create in the worst case an impurity layer comparable (same order of magnitude) to the total lithium content of samples. Although no LID analyses were performed in order to search oxygen or water desorption from impurities (Li oxides or hydroxides), the SIMS results showed a very low presence of such impurities compared to lithium (see section 3.2.2 for further details), hence the formation of impurities on the Li layer during the pumping periods can be considered as not very significant.

Different LID analyses were performed on the sample, changing the position of the laser spot and the gaseous species that is measured ($D_2$, $H_2$, HD). With the RGA measurements to get enough time resolution ($\approx 70$ ms) of the desorption peaks, the device must be operated in the leak test mode. In this mode, only one species can be measured in each laser shot. Consequently it was no possible to measure the content of more than one molecule at the same point of the sample. Therefore, the determination of the different hydrogenic species must be carried out in different points of the samples. Differences on the Li/hydrogenic content depending on the position of the samples are expected as a result of the
non-homogeneous deposition of lithium on sample and the concomitant deuterium absorption. Several measurements for each hydrogenic molecule were performed to average the results. In each laser spot the irradiation is repeated several times until the residual peaks obtained by the RGA are smaller than the 5% of the first peak. These peaks are attributed to lateral propagation of the laser radiation that induces hydrogenic desorption from adjacent (lateral) points to the laser spot. At this moment, it is considered that the total desorption on the spot has taken place. Normally it happened after 2–3 laser shots on the sample spot. In the samples with highest lithium content, that made possible its direct easy visualization (e.g. wlid6), the removal of the whole lithium layer on the laser spots was clearly visible after this procedure, thus indicating the concomitant full removal of deuterium, that posteriorly was corroborated by the morphology of the LID craters (see profilometry section, numbered as 3.2.3).

By calibrating absolutely the mass to charge ratio, the signals associated to the hydrogenic molecules (2 amu/e for H₂, 3 amu/e for HD and 4 amu/e for D₂) can be quantified. This work (calibrated leak method) relates the single RGA peaks to absolute flux values (molecules/s) allowing the absolute quantification of the desorbed products. The concomitant mass to charge ratio signal, obtained by subtracting previously the background level of the signal with no input flux into the chamber, can be translated to molecular flow. By integrating the peaks registered by the RGA the retained hydrogenic content can be absolutely quantified. This calibration procedure was performed separately for hydrogen (calibration respect to 2 amu/e) and deuterium (respect to 4 amu/e). For the mixed specie, as pure HD gas bottles were not available at laboratory, the absolute calibration cannot be performed. Consequently for HD, an intermediate value between the calibration constants for hydrogen and deuterium was used in the quantification. During the RGA measurements associated to LID a special care was taken to ensure a sampling rate fast enough (~70 ms) to not distort the temporal shape of the desorbed peaks. Figure 4 shows that the RGA obtained signal is quasi-coincident compared with the corresponding pressure signal (Ionization gauge sensor) measured with a faster sampling rate (5 ms) during the desorption induced by the laser shot, thus confirming a proper RGA data sampling.

### 2.3. Post-mortem analyzes on samples

#### 2.3.1. Thermal desorption spectroscopy (TDS)

In order to compare the retention values obtained by LID with other absolute quantification technique, TDS analyses assisted with mass spectrometry (RGA measurements) were implemented on the samples wlid11 and wlid13 after its LID irradiation. Again, the samples transportation was the same previously detailed to avoid atmospheric contamination. Inside the deposition chamber, the samples were heated up by using the tungsten filament described in section 2.1.1. The surface temperature of the sample was measured with the optical pyrometer and desorption was followed registering the changes on the chamber pressure with an ionization gauge. Additionally, a SRS 100 mass spectrometer, identical to the previous one used in the LID measurements, was installed in the deposition chamber trying to follow the thermal desorption. Unfortunately the increase in the pressure produced the saturation of the RGA filament and the failure in the mensuration. Before starting the TDS measurement, the W filament used for the sample heating was outgassed by feeding it with the maximum power during 30 min in order to eliminate water, hydrogenic molecules or another volatile species that could disturb the changes in the pressure measured during the analysis. This outgassing was performed with the sample situated in a completely retracted position along the manipulator to maintain it at room temperature and not produce any desorption from it due to residual heating induced by the filament. In this way, the increase in the pressure can be approximated as produced mostly due to the deuterium desorption that are the majority volatile component of samples, giving the result a maximum limit for the deuterium retention. Finally, a calibration work for the absolute pressure signal respect to deuterium fluxes introduced in the chamber (equivalent to the explained in section 2.2) was performed to absolutely quantify the deuterium retention.

#### 2.3.2. SIMS analyzes

SIMS measurements were carried out on three samples: the wlid6 sample (pre-lithiated and exposed to deuterium at 200°C), the wlid8 sample (pre-lithiated and exposed to D₂ at 300°C) and the wlid12 sample (blank). Transportation of the samples from LID to SIMS vacuum chambers was carried out by using the same procedure previously explained for the LID analyzes with the used manipulator over-pressurized with dry argon. To identify the elements and compounds present on the sample surface layer a static SIMS analysis (mass to charge ratio scan, m/q) was performed as the first step of the analytical procedure.

Two different mass scans were performed. The first one from 0 to 80 amu/e, in order to identify hydrogenic species (H₂ at 2 amu/e, HD at 3 amu/e and D₂ at 4 amu/e), Li isotopes (⁶Li and ⁷Li), oxygen from the ion beam, residual
water molecules (amu/e 18–20) and the presence of Li impurities due to the atmospheric contamination: lithium oxides (amu/e 28–30 and LiO clusters from oxide cracking at amu/e 22–23), lithium hydroxides (amu/e 23–25) and lithium carbonates (amu/e 72–74). The second mass scan covered the amu/e range from 180 to 220 in order to recognize the W isotopes (amu/e 182–186) and the possible associated oxides (amu/e 198–202) and lithium combinations (amu/e 188–193). After the identification of the main elements and compounds, dynamic SIMS analyses were performed in order to study the depth profiles of the more interesting constituents. Among the several mass to charge signals measured in this dynamic SIMS, four of them were particularly interesting due to the lack of overlapping with other isotopologue species: 4 amu/e that is directly related with D₂, 6 amu/e (⁶Li), 9 amu/e (³LiD) and 184 amu/e (¹⁸⁴W). Both static and dynamic (with simple electrostatic quadrupole detection) SIMS analyses were performed with O⁺ primary ion beam in a Hiden SIMS Workstation experimental unit. The residual vacuum determined a pressure around \(5 \times 10^{-5}\) Pa inside the chamber during the measurements, while the characteristics of the primary ion beam were a nominal emission current of 500 nA and beam energy of 5 keV.

### 2.3.3. Profilemetry measurements.

This technique was used to estimate the size (diameter) of the LID craters. Furthermore, other measurements were performed in order to estimate the thickness of the lithium layer deposited on tungsten comparing the level of this Li layer to the (lithium free) W surface situated below the sample holder table used for the sample fastening during its Li–D₂ exposure. In principle, small deviations and/or inclinations in the sample surface can exist. However, the profilometer software was equipped with a specific tool for the (virtual) alignment of the crater lateral boundaries as well as the alignment of remaining Li surface in the case of the involved Li thickness measurements. This alignment protocol was carried out before starting the profilometry analysis. In this way, the obtained results cannot be attributed to any sample surface inclination and/or deviation. These profilometry measurements were carried out in atmospheric conditions without protecting the lithium films from contamination. No chance of performing them on a vacuum environment was possible. For the measurements a 2D stylus profilometer (Bruker DektakXT) with a vertical resolution of 1 nm was used. A picture of a LID crater present on the W–Li surface of a sample is represented in figure 5. Although in the figure the geometrical shape of the crater seems ellipsoidal due to the picture deformation induced by the perspective of the profilometer camera lens, specific measurements of the diameter in both X and Y axis shown that the craters were approximately circular.

### 2.3.4. Flame atomic emission spectrometry (FAES) for quantification of the deposited lithium.

After the application of these techniques, aqueous Li dissolutions were prepared by immersing the W–Li samples in 50 ml of hot ultrapure (Milli-Q) water. Then, they were sent to the chemistry laboratory that carried out the FAES analysis to determine the total lithium content of the samples. This procedure was performed for the wild (simultaneously exposed to Li–D₂ environment) and the pre-lithiated (wlid6, wlid8, wlid10, wlid11 and wlid13) samples. Furthermore, other samples were prepared for FAES determination in order to compare the formation of the lithium film on the W surfaces depending on the deposition conditions (gas presence or absence, pressure and surface temperature). Two different sets of additional samples were prepared:

- Samples exposed to lithium evaporation in high vacuum conditions (\(p \approx 6 \times 10^{-5}\) Pa). The evaporation also took place at 450 °C in the lithium oven. Three samples were prepared at different \(T_{\text{surface}}\): 200 °C, 300 °C and 400 °C. These samples were not later exposed to any D₂ exposure, thus avoiding the concomitant and additional surface heating that eliminates a part of the lithium film due to its melting and dripping. In this way the removal of lithium due these effects can be directly evaluated by comparing the lithium thickness in this group of samples with the obtained for the pre-lithiated samples.

- Samples exposed to lithium deposition under a helium atmosphere at \(p = 0.67\) Pa. Evaporation of lithium was carried out under the identical conditions employed for the preparation of the wild sample but changing the D₂ atmosphere by helium one, in order to compare the influence of the presence of an inert gas instead of D₂ that in principle can interact with the lithium atoms. Different samples were prepared at surface temperatures of 200 °C, 300 °C, 400 °C and 500 °C.
3. Experimental results

3.1. Deuterium and hydrogen retention by LID

The number of hydrogenic molecules desorbed from the irradiated sample spots is calculated by integrating the registered RGA peaks over the time and summing these integrated peaks as these equations show:

\[
H_2^{\text{des}} = K_{H2} \cdot \sum_{i=1}^{n} \int (2 \text{ amu/e} - \text{background}) \cdot dt,
\]

\[
HD^{\text{des}} = K_{HD} \cdot \sum_{i=1}^{n} \int (3 \text{ amu/e} - \text{background}) \cdot dt,
\]

\[
D_2^{\text{des}} = K_{D2} \cdot \sum_{i=1}^{n} \int (4 \text{ amu/e} - \text{background}) \cdot dt,
\]

being \(K_{D2}, K_{H2}, \) and \(K_{HD}\) the values of the calibration constants for \(D_2, H_2,\) and \(HD.\) With these values, the hydrogenic areal densities are directly obtained with the equations (5) and (6):

\[
D_{\text{ret}} = \frac{2 \cdot D_2^{\text{des}} + HD^{\text{des}}}{A_{\text{spot}}},
\]

\[
H_{\text{ret}} = \frac{2 \cdot H_2^{\text{des}} + HD^{\text{des}}}{A_{\text{spot}}}.
\]

The profilometry measurements (see section 3.2.3) yielded a mean spot diameter of 0.125 cm. Hence, by considering it as approximately circular, the desorption area is \(A_{\text{spot}} \approx 0.0123 \text{ cm}^2.\) To obtain the retention values for hydrogen and deuterium (\(H_{\text{ret}}\) and \(D_{\text{ret}}\)) several sample points were analysed with the laser beam. Normally four or five zones were irradiated looking for the signal 4 amu/e in order to measure the \(D_2\) (main constituent) content depending on the sample position. Two points were used to measure the HD content and another two for the \(H_2\) content. The results were averaged taking into account all the irradiated spots. This procedure was carried out for the samples wld6, wld11, wld13, wld11 and wld13. With this method the hydrogenic content is measured in all the regions of the sample. An example of the experimental details and the desorbed values obtained in the laser shots performed on the wld6 sample is presented and table 2. Additionally, figure 6 shows the aspect of the sample wld11 inside the LID chamber after applying the laser shots. In this picture, the laser spots are perfectly visible showing the removal of the lithium layer due to the pulsed laser heating. As the SIMS analyses also showed a hydrogenic content associated to the lithium layer (see section 3.2.2), the total removal of lithium would be associated to the complete desorption of the hydrogenic content. This consideration is corroborated by the profilometry results that will be presented in section 3.2.3. They also indicated a LID crater surface with lithium absence induced by the laser heating of the Li–D film.

As the laser pulse duration was 0.25 milliseconds, the heating of the side areas placed beyond crater boundaries was probably produced. As was commented in section 2.2, the LID procedure normally consisted in three laser pulses irradiated on each sample point. As a result of this multiple laser heating and the irregular (not perfectly Gaussian) laser profile, the non-homogeneous heating of the spot and the diffusion of a part of the hydrogenic molecules from the LID crater to their boundaries can occur. Consequently, the associated trapping of hydrogenic particles on these zones could prevent the desorption and LID detection of the related hydrogenic content. However as the vast majority (85–90%) of the hydrogenic content was desorbed during the first shot (see figure 7), it seems logical to think that the subsequent diffusion during the additional LID shots did not produce a significant loss in the hydrogenic measurement. Additionally, the matrix effect produced by the repeated laser shots could contribute to disturb the desorption process of a part of the retained hydrogenic species. However the observation that the majority of the hydrogenic content was released during the first laser pulse seems to indicate that the contribution of this matrix effect can be also considered as non-significant. Related to this particularity, it is also important to mention that the profilometry analyses performed on the LID craters showed a smooth surface without the irregular morphology associated to Li content (see section 3.2.3 and figure 14) thus indicating the total removal of the Li–D content on such surface. Additionally,

### Table 2. LID analyzes on wld6 sample.

| LID point | Analyzed molecule | Spot position | Desorbed molecules |
|-----------|-------------------|---------------|-------------------|
| 1         | D₂ (4 amu/e)      | Left lower corner | 1.70 \times 10^{16} |
| 2         | D₂ (4 amu/e)      | Right lower corner | 9.82 \times 10^{15} |
| 3         | D₂ (4 amu/e)      | Right upper corner | 6.33 \times 10^{15} |
| 4         | D₂ (4 amu/e)      | Upper center | 1.18 \times 10^{16} |
| 5         | D₂ (4 amu/e)      | Center | 9.76 \times 10^{15} |
| 6         | HD (3 amu/e)      | Left center | 2.12 \times 10^{15} |
| 7         | HD (3 amu/e)      | Lower center | 1.58 \times 10^{15} |
| 8         | H₂ (2 amu/e)      | Right center | 4.98 \times 10^{14} |
| 9         | H₂ (2 amu/e)      | Left upper corner | 6.96 \times 10^{14} |

![Figure 6. Picture of the sample wld11 situated inside the LID chamber. The spots present on the sample surface (produced by the LID shots) show the complete removal of the Li–D layer.](image-url)
3.2. Post mortem analysis for W–Li–D film characterization

3.2.1. Thermal desorption spectroscopy. Figure 8 shows the result of the TDS analysis performed on the sample wlid11. The heating rate during the first instants of the analysis was around 11 K s$^{-1}$. A maximum temperature of 570 °C was reached on the sample surface. Two clear peaks are visible in the TDS spectrum, the first and bigger one at 500 °C of surface temperature and the second one (smaller) at 550 °C, being these results in agreement with previous findings in TDS experiments performed on W–Li films [14]. Assuming that water, hydrogen and other impurity contributions are negligible, the deuterium retention resulted in $1.3 \cdot 10^{18}$ cm$^{-2}$, value that agrees reasonably with the LID results ($2.0 \cdot 10^{18}$ cm$^{-2}$), being them comparable. Theoretically, the total decomposition of pure lithium hydride (mostly LiD in this case) takes place at temperatures close to 700 °C. For LiD–Li mixtures the decomposition temperature for the hydride depends on the external pressure [13]. As the maximum temperature achieved by the sample during the TDS is 570 °C, some lithium deuteride particles could remain on the surface after the TDS, thus explaining the lower deuterium retention values obtained by TDS compared to the obtained by LID. However, under high vacuum conditions (very low D pressure) the LiD molecules can be depleted at lower temperatures [12, 13], showing these results total D release at similar temperature to the reached during this TDS experiment. In any case, although this TDS global value is smaller, it is necessary to take into account that deposition of lithium and the concomitant D uptake on the W–Li films were not homogeneous (see profilometry results section, numbered as 3.2.3). Moreover, the LID technique could induce desorption from adjacent parts of the treated spot, thus including a bigger desorption area and producing an overestimation of the obtained deuterium retention. To investigate the possible presence of deuterium (mainly in the form of LiD) after the TDS, the sample wlid11 was transported again, following the protocol to avoid its contamination, to the LID chamber in order to corroborate the total hydrogenic removal on the sample by the TDS technique. Several LID shots were implemented on the outgassed surface to measure desorption of the different hydrogenic species. While no desorption of D$_2$ and HD related peaks was visible, tiny H$_2$ related peaks, that are probably related to the unavoidable contamination with the residual vacuum during pumping period prior to the new LID measurement, were obtained resulting on values of $H_{\text{res}} = 3 \cdot 10^{14}$ cm$^{-2}$. These results imply:

- Total deuterium removal and no LiD remaining on the whole sample after TDS.
99.9% of hydrogen removal on the sample with a maximum surface temperature of 570 °C induced by TDS.

Differences between global (TDS) and local (LID) deuterium retention values that could be explained by the limited accuracy related with the TDS measurements, the inhomogeneity of the films, the overestimation of the LID desorption area or other experimental uncertainties.

3.2.2. SIMS analysis. Figure 9 presents the mass scan for light elements (0–80 amu/e) performed for the sample with highest Li/D content (wlid6). It shows the presence of hydrogenic molecules and Li isotopes in high intensity peaks that even saturate due to the high content on the sample and the high sensitivity of the SIMS detector for these species. Another big peaks present at 12–14 amu/e can correspond to the detection of Li2 clusters formed on the beam plume. Although on this sample the lithium content was the highest and consequently, the concomitant associated impurity content is probably the larger, the presence of Li oxides resulted minority as the associated peaks (amu/e 28–30) are small. There is no presence of lithium hydroxides and carbonates peaks. It demonstrates that the conservation and transportation of the samples during all the experimental procedure was adequate, avoiding the significant contamination of the Li–D containing films. Figure 10 shows a second mass scan covering the m/q range from 180 to 220 in order to recognize the W isotopes (amu/e 182–186) and the possible associated oxides (amu/e 198–202) and lithium combinations (amu/e 182, 183, 184 and 186) are visible, belonging the highest peak signal to 184W. Small peaks associated to the combination of lithium isotopes with tungsten (amu/e 189–191 and 193) and tungsten oxides (amu/e 196–200 and 202) are also visible. These clusters can be produced as a result of the interaction of sputtered W and Li atoms with the oxygen ions in the beam plume.

Table 3. Hydrogenic retention results for the samples analyzed with LID.

| Sample         | D2-Li exposure | Tsurface, °C | Hret, cm−2 | Dret, cm−2 |
|----------------|----------------|--------------|------------|------------|
| Wlid           | D2-Li co-deposition | 225         | 2.6 ± 0.6 · 1016 | —          |
| wlid6          | pre-Li + D2     | 200          | 2.4 ± 0.8 · 1017 | 1.9 ± 0.7 · 1018 |
| wlid8          | pre-Li + D2     | 300          | 4.4 ± 0.9 · 1015 | 1.5 ± 0.3 · 1015 |
| wlid10         | pre-Li + D2     | 400          | 1.3 ± 0.4 · 1015 | 4.3 ± 0.4 · 1015 |
| wlid11         | pre-Li + D2     | 200          | 5.9 ± 1.4 · 1017 | 2.0 ± 0.3 · 1018 |
| wlid13         | pre-Li + D2     | 200          | 2.8 ± 0.5 · 1017 | 2.0 ± 0.6 · 1018 |
| wlid12         | no Li–W blank   | 200          | —          | —          |

Figure 9. Static SIMS on wlid6 sample: mass scan from 0 to 80 amu/e.
signals. Assuming RSF values not very different for lithium and their impurities, it is logical to think that the impurity content is much lower compared to lithium. The corresponding mass scan from 180 to 220 amu/e also showed the peaks associated to W isotopes and their oxides but not the W–Li cluster peaks. It could be related with the smaller lithium concentration on sample, experimental fact that is corroborated by the dynamic SIMS results that is shown in figure 11.

For the blank W sample, some peaks showed the presence of lithium. However, no deposition of lithium was performed during the sample preparation. Probably this detection was produced due to previous contamination of the chamber. The level of lithium contaminated compounds (oxides, hydroxides...) was also negligible. In the second static SIMS on this sample the W peaks and their oxides dominated the spectrum while associated lithium was not detected, thus pointing to the formation of W–Li clusters in the beam plume after the sputtering of these species induced by the impinging beam. As the blank sample does not present any Li content on surface, these W–Li clusters cannot be formed and consequently they did not appear in the static SIMS spectrum.

Figure 11 presents the comparative dynamic SIMS results for the non-overlapping signals on the sample wlid6, wlid8 and the W reference sample (wlid12). In this plot the signals are normalized to the signal at 16 amu/e that corresponds to the oxygen primary ion beam used for the analysis, in order to detect differences in the ion beam fluence that could affect to the extracted results. The highest content in Li and D for the wlid6 sample is clearly visible. Comparing the both pre-lithiated samples, the intensity of the Li and D2 signals is one order of magnitude higher in wlid6. Moreover, the temporal evolution suggests that the Li–D thickness of the wlid6 sample is at least larger by one order of magnitude compared to the wlid8 sample as the analysis time necessary for the saturation of the involved signals is a factor 20 greater. Respect to the signal related with lithium deuteride (Li7D at 9 amu/e) it presents a significant intensity for the wlid6 sample being this signal much bigger compared to wlid8. Consequently the presence of LiD in the W–Li film seems evident. For wlid8 the signal is at the same level as the W blank (noise level), thus suggesting the absence of lithium deuteride in this sample. The normalized profiles of D2 and Li for samples wlid6 and wlid8 are presented in figure 12 in order to correlate Li and D2 depth profiles on the sample and study the chemical interaction and association of both elements. The figure shows completely coincident profiles for Li and D2 in both samples.
It reveals deuterium retention on samples associated to the lithium layer present on the surface.

Finally although the SIMS technique does not allow an easy and direct absolute quantification of the components, as the absolute calibration of this technique is extremely challenging and requires specialized standards, the dynamic results shown in the previous figures were normalized to the W$^{184}$ profile obtained for the wlid12 (W blank) sample. This procedure allows an approximate and relative semi-quantification of the D content by the comparison of the profiles for wlid6 and wlid8. The results of this analysis are represented in figure 13.

The comparison of the normalized D$_2$ profiles for wlid6 and wlid8 reveals values of the D$_2$ signal normalized to W that are a factor 20–100 times higher for the case of wlid6 sample. Furthermore, the necessary time for the saturation of the D$_2$ related signal is larger (factor 25) for wlid6 sample. These results would indicate a dramatically lower D uptake in the case of wlid8 sample that could be roughly estimated as a difference in a factor 500–2500. The LID results indicated absolute D content (1300 lower) in wlid8 sample. Consequently, the SIMS analyses qualitatively corroborate the absolute quantification of the LID technique. Additionally, they indicate important results about the composition of the W–Li films:

- Presence of lithium deuteride in the sample wlid6 (exposed to D$_2$ at 200 °C), but not in the sample wlid8 (pre-lithiated and exposed to D$_2$ at 300 °C).
- Very low contamination of the samples with lithium oxides and hydroxides.
- Association of deuterium to lithium in the studied films.

### 3.2.3. Profilometry measurements

The vast majority of the LID produced craters were measured by profilometry. Additionally, the remaining Li–D layer present of the sample surface that was not irradiated by the laser was also measured in order to study the morphology and the thickness of the Li films. It is important to note that the laser beam irradiation was able to produce craters on the Li surface of the Li containing samples, but not on the W surface of the samples where lithium was not deposited. This experimental fact was observed in the case of the blank tungsten (sample wlid12). For future experiments, however, it seems interesting try to irradiate other samples (perhaps containing CH films) in order to compare the morphology of the LID produced craters and the concomitant spots produced by our laser by using post-mortem profilometry.

As a consequence of the experimental LID procedure, where 2–3 laser shots were applied to each sample point in order to remove all the hydrogenic content, the measured crater diameters were probably a little larger compared to the created after a single shot. It is important to remember that these analyses were carried out in atmospheric conditions. Under such conditions, the lithium films were transformed into lithium carbonate (Li$_2$CO$_3$). Lithium carbonate films are affected by swelling effects induced by its high hygroscopic activity, thus altering (increasing) the thickness and the state of the Li films. Consequently the estimation of the real (original) lithium film thickness was not possible. The Li film surface measurements showed a irregular morphology with pronounced spikes and valleys. The height of these surface spikes resulted substantially larger compared to the lithium average thickness obtained by FAES, (see section 3.2.4) due to the previously commented swelling effects. This irregular deposition originated the presence on the sample of zones with intense lithium coverage together with other with Li shortage. As these analyses were carried out after applying the alignment protocol, this irregular morphology did not result of any sample inclination and hence the measured irregular morphology surface was likely
produced due to the irregular Li deposition and the swelling effects derived from the carbonate formation. Regarding the crater diameter measurements, as all the surface is assumed to be homogeneously attacked, the footprint of the LID crater size (diameter) can be considered unaltered. Moreover the interior surface of the LID crater did not present the characteristic irregular surface, with spikes and valleys, characteristic of the adjacent sample zones not-treated with Li that is associated to the Li presence, thus assuring the total Li, and concomitant hydrogenic, removal on the LID spots during the laser irradiation. An example of the profilometry measurements can be visualized in figure 14. Averaging the profilometry results for all the measured craters in the treated samples, a nominal value for the laser spot diameter was obtained:

\[ d_{\text{spot}} = 0.125 \pm 0.008 \text{ cm} \]

3.2.4. Quantification of lithium content on samples by FAES. Estimations of lithium film thickness. The results of the Li thickness determination for all these samples are represented in table 4. The conversion of the FAES determinations (lithium concentration, \([c_{\text{Li}}]\) in mg/L) to average lithium thickness originally present on sample is performed taking into account the volume (V) of the prepared lithium dissolution (50 cm³), the area of the sample (3.6 cm²) and the density (0.534 g cm⁻³) of lithium:

\[ \delta_{\text{Li}} = \frac{[c_{\text{Li}}] \cdot V}{A_{\text{sample}} \cdot \rho_{\text{Li}}} \quad (7) \]

Additionally, it is necessary to take into account that LID (and also SIMS) is a destructive technique that implied the removal of a (small) part of the lithium layer before the FAES measurements. The measured diameter of the LID craters resulted 1.25 mm and their area 0.0123 cm². As and the total number of analyzed spots in each sample were normally 8, hence, the total lost area due to LID analyzes, is \(\approx 0.098\) cm². The SIMS spots were much smaller compared to the LIDS ones (<0.5 mm of diameter) and for all practical purposes they can be considered totally negligible. Taking into account the removed area associated with the LIDS spots and the total sample area covered by lithium (3.6 cm²), this ‘lost area’ and the concomitant lost mass is around 2.7% of the total. These lithium losses were added to the total amount determined by FAES.

In order to globally analyse the Li uptake obtained for the different samples, in principle, the incident lithium flux to the deposition areas from evaporative sources depends on the surrounding pressure that affects to the mean free path (\(\lambda\)) of Li atoms. This parameter is influenced by the collisions of the Li atoms with the gas particles present in the chamber during the evaporation and can be considered as inversely proportional to the pressure. A detailed calculation taking into account these effects can be found in [41]. However, an exhaustive analysis of the lithiation environment dependency on the Li deposition thickness is out of the scope of this work. The second factor that influences the Li uptake by the tungsten sample is the surface temperature. Melting point of lithium is 180.5 °C. Beyond this temperature, lithium atoms will be in liquid state and the vertical configuration of the sample can induce the slipping and dripping of lithium that decreases the net uptake. Moreover, at temperatures higher than 350 °C the evaporation of lithium from the sample surface begin to affect to the deposition, as the remaining Li atoms can be evaporated in a significant fraction that will increase exponentially with the surface temperature. At lower temperatures the evaporation rate on the sample surface can be considered as negligible. Hence, beyond 350 °C on the sample a competition regime between the deposition of Li atoms from the oven and the evaporation of Li on the hot sample surface would be achieved. Comparing the results of the FAES analysis for different \(T_{\text{surface}}\), at the same deposition conditions, a clear trend is visible for all the samples independently of the deposition type. The Li deposited thickness decreases at higher temperatures, being the obtained values an order of magnitude lower for temperatures of 400 °C compared to the case of 200–225 °C. At this point, the global quantification of the evaporation, dripping and slipping, for the pre-lithiated samples, effects with surface temperature and the direct comparison between different samples seems difficult to evaluate. Nonetheless, the found effect of the surface temperature in the Li film formation is clear and has great importance, as a \(T_{\text{surface}} = 400\) °C, for the Li deposition or for the subsequent D₂ exposure, determines very thin lithium films (<100 nm) on the tungsten substrate for all the studied experimental conditions, thus precluding the potential formation of thick Li co-deposits on the W surfaces of plasma shadowed or remote zones that could be specially problematic in a fusion reactor combining liquid Li and W PFMs.

3.3. General summary of the experimental results

The global quantitative results obtained from all the experiments and analyses are presented in table 5. After the quantitative and qualitative evaluation of the totality of them, the following experimental findings can be extracted:

- The LID technique has been developed for fuel removal and retention measurements (absolute quantification)
in W–Li films exposed to molecular deuterium. A $T_{\text{rise}} > 600 \text{K}$ for the whole sample during the LiD pulse is obtained from simulations. Additionally the total Li removal in the irradiated spots was visualized with profilometry. The SIMS measurements also established that the hydrogenic content is associated to the Li layer, thus assuring the total elimination of such species during the laser irradiation.

- The D uptake on W (at 225 °C) exposed simultaneously to Li and D$_2$ in a so-called thermal co-deposition regime (simultaneous deposition of Li and D$_2$) is below the limit of detection of the LID technique, being the measured global D interaction for a Li film with 2 µm at the same level compared to the retention measured on the pure tungsten sample (wld12).

- For the case of the pre-lithiation + D$_2$ exposure sample preparation regime the three values obtained for D$_{\text{ret}}$ at 200 °C are very reproducible ($\approx 2.0 \cdot 10^{-19}$ cm$^{-2}$).

- In this regime, the D retention exhibits a strong (non-linear) dependence with the surface temperature on sample. At 300 °C, the D$_{\text{ret}}$ is reduced in a factor 1300, while at higher temperatures (400 °C) the amount of D atoms retained on the W–Li layer is decreased in a factor 50,000 compared to the case of $T_{\text{surface}} = 200$ °C. Hence, the Li–D interaction in liquid thin films deposited on W is substantially reduced for $T_{\text{surface}} \geq 300$ °C.

- About the hydrogen retention measurements, as the samples were not exposed directly to hydrogen, this content should be related with the presence of impurities on the Li films. This experimental fact is likely produced due to the unavoidable interaction of the lithium films with the residual vacuum, and more specifically with residual water, during the experimental procedure (oven cooling time for pre-lithiated samples and pumping time prior to LID for all samples) widely explained in sections 2.1.2 and 2.1.3. For the case of the wld12 sample (W blank without Li content), no measurable values were obtained for H$_2$ retention. This observation points to the impurity growth associated to the interaction of the residual vacuum with lithium as the main cause of this hydrogen content observed in lithium containing samples.

- The deuterium content is also related with the lithium coverage. The subsequent sample heating during the D$_2$ exposure produces the melting and dripping of Li in the pre-lithiated samples, thus determining the formation of a thinner lithium film. This observed Li layer reduction, however, cannot totally explain the drastic differences in terms of retention found for the pre-lithiated samples exposed to D$_2$ at different temperatures.

- The thickness of the liquid lithium film formed on W also depends on the experimental conditions (surrounding pressure, flow regime, presence of different gas species and surface temperature). In any case a surface temperature of 400 °C, during the Li exposure or during the subsequent D$_2$ exposure for the pre-lithiated samples, determines a very thin Li film on the W substrate ($\leq 100$ nm).

- The relative semi-quantification of the W–Li–D films performed with SIMS analyses corroborates the LID retention results in terms of D retention. SIMS also showed a low content of associated impurities (oxides and hydroxides) besides an absence of carbones in the lithium films.

- TDS ($T_{\text{max}} = 570$ °C, 10') also allows the total removal of deuterium and hydrogen from samples, being the absolute retention results comparable to the values obtained by LID.
4. Global discussion of the obtained results. Implications for an innovative fusion reactor design based on a liquid Li divertor combined with a W first wall

4.1. Thermodynamic aspects of the thermal deuterium absorption in thin Li films deposited on W

The characterization and analysis of the W–Li–D films performed in this study reveals a strong, non-linear effect of the increasing surface temperature on the D uptake at $T_{\text{surface}} \geq 300 ^\circ \text{C}$. The global results presented in table 5 allow analysing the role of lithium coverage and surface temperature on the global D uptake for the pre-lithiated samples later exposed to D$_2$. Comparing the Li uptake in the samples wlid6 and wlid8, a decrease in a factor 15 is found for the case of $T_{\text{surface}} = 300 ^\circ \text{C}$. The additional heating necessary for the subsequent D$_2$ exposure after pre-lithiation leads to Li removal by dripping and slipping of the liquid layer. Additionally, the Li content on the sample wlid10 ($T_{\text{surface}} = 400 ^\circ \text{C}$) is a bit higher compared to the sample wlid8. In principle the lithium losses due to the effects of increasing temperatures will be larger at higher temperatures, hence it seems that the quantification of the global effects of the temperature (evaporation, dripping and slipping) in the Li losses are not evident, as other experimental factors (as presence of cold parts on surface, formation of lithium aggregates due to surface tension and forces, etc) and uncertainties can have an influence. In any case it is clearly visible that even for the case of a $T_{\text{surface}} = 300 ^\circ \text{C}$ (sample wlid8) the decrease in the lithium content (factor 15) on sample is not proportional to the reduction in the D retention (factor 1300) thus suggesting that the interaction of Li deposited atoms with thermal deuterium molecules is affected and reduced with increasing surface temperatures. This assumption is corroborated by the results obtained for the wlid10 sample ($T_{\text{surface}} = 400 ^\circ \text{C}$). As was explained previously, the lithium uptake at this temperature is not reduced compared to the pre-lithiated sample exposed to D$_2$ at 300 °C (wlid8). However the D uptake is a factor 35 lower. Consequently, the changes induced by increasing the surface temperature in the Li–D surface chemistry (that determines the adsorption and/or bonding of the deuterium atoms to the Li film) seems to be the most important factor that determines the drastically lower retention values obtained at increasing temperatures.

In this way, the D uptake dependence with $T_{\text{surface}}$ by the Li films deposited on tungsten would be influenced by two factors: a lower Li deposition and a reduced D uptake by the lithium atoms present on the created liquid thin film at higher temperatures, thus resulting in a synergistic combined effect that could explain the temperature dependence of the results and the extremely lower retention values measured by LID at 400 °C. In figure 15, an Arrhenius-type plot of the D/Li ratio is shown for the three pre-lithiated samples (wlid6, wlid8 and wlid10). Assuming that the release of deuterium from the film can be characterized by a specific activation energy, a value of $E_a = 1.4 \text{eV}$ is obtained for the process. This value is smaller than the activation energy for lithium hydride decomposition (2.0 eV [42]), and 7 times higher than the heat of solution deduced from the T dependence of the H solubility [43], perhaps suggesting an intrinsic dependence of the D/Li ratio on the film thickness itself. However it must be noted that this result is limited to only three experimental cases. Additional experiments (at different temperatures) would be necessary to confirm this observation.

Comparing the retention rate (D/Li atomic ratio) observed in these samples with the solubility data for deuterium in lithium bulk [44], the obtained result at 400 °C after 1 h of exposure to D$_2$ is much lower, more than two orders of magnitude, compared to the equilibrium concentrations. In this respect, it is worth noting that the pressure of D$_2$ used in our experiments is far larger than the expected near the remote or plasma shadowed parts of the first wall of a reactor. Thus, for 400 °C, the equilibrium pressure, that corresponds to the onset of hydride formation, is $\approx 10^{-2}$ Pa and still, even with $P = 133$ Pa, a value of D/Li more than two orders of magnitude lower than the saturated solubility limit of $\approx 1\%$, was recorded at this temperature. For the sample exposed at 200 °C the retention measured is higher than the equilibrium value, thus corroborating the formation of LiD after overlapping the saturation in the deuterium solution. Finally, the sample exposed at 300 °C presented a retention value in the order of the solubility equilibrium. According to these results, the thermodynamic behaviour of liquid lithium thin films deposited on W in terms of hydrogenic absorption seems to be different compared to the case of liquid bulk absorption thus resulting in a reduced hydrogenic uptake at temperatures higher than 300 °C. Finally, regarding to the sample prepared under a Li–D$_2$ simultaneous exposition regime, the obtained results at low (225 °C) wall temperature indicated a negligible D retention on the liquid Li film (h$_{\text{Li}} \approx 2 \mu\text{m}$) comparable to the case of pure W. Taking into account the previously inferred results about the temperature effect in the D retention on the W–Li pre-deposited films, it seems logical to think that at $T_{\text{surface}} \geq 400$ °C, that constitutes a scenario for the proposed DEMO operation with hot W first wall, the fuel uptake associated to thermal simultaneous Li–D$_2$ deposition of deuterium and lithium on W would be even more reduced.

The lessons learned from this extensive experimental work are important for the evaluation of the problematic related with potential first wall zones situated far away from the divertor or plasma shadowed, where the involved Li and fuel uptake mechanisms can be similar to that used in the preparation of...
the thin liquid Li–D films that have been studied. These zones can be prone to thick thermal Li deposition, whose associated fuel retention could be dangerously intense. Our results have shown that an operation at $T_{\text{surface}} = 400 \ ^\circ\text{C}$ could drastically diminish the problem.

4.2. Considerations for the fuel retention associated to the W first wall in a reactor scenario with the proposed PFM solution

At this point it is worth to assess the implications of the present results in the hypothetic operation of a DEMO-like reactor under a liquid lithium target divertor/hot W first wall scenario. For this purpose, the more important aspects in order to evaluate and compare our experimental results, in terms of Li and D retention on W, to DEMO-like conditions are related to the real Li–D fluxes expected in a reactor scenario.

Firstly, regarding the Li impurity flux, at the considered evaporative temperature of 450 °C, the associated Li evaporative fluxes, that supposes the problematic approached in this work, will dominate this scenario [16, 23]. The experimental preparation of the samples took into account this dominant contribution for the lithium deposition as the samples were vertically located close to the Li source (oven) that simulated the liquid Li divertor. Consequently, the comparison of the (thermal) lithium uptake found for the samples compared to the hypothetical one that can be expected in vertical zones of the first wall situated away from the divertor and/ or plasma shadowed seems reasonable. As was commented in section 3.2.4, the Li uptake due to effusive fluxes strongly depends (inversely) on the surrounding pressure, as well as on the inverse-square of the distance from the Li source. The pressure levels existing in the divertor region would determine a lower Li uptake on the first wall zones situated far away from the divertor as is explained in [41]. Consequently it is quite likely that the first wall areas, that potentially suppose the object of study of this work, will not be exposed to higher pure evaporative lithium fluxes compared to the samples studied in our experiments. For the case of the Li impurity flux due to the sputtering contribution, that has not been approached in our experiments, a rigorous study showed [21] that in liquid state, approximately 65% of the Li sputtering by hydrogenic bombardment is in the form of Li ions. The electromagnetic forces generated at the SOL/plasma edge and acting on the Li ions can affect the transport/migration of such ions from the plasma boundary to the PFCs surface, perhaps minimizing the deposition on W of this fraction of sputtered Li ions. In any case, a part of the Li+ ejected atoms, the sputtered neutral Li and a fraction of evaporated lithium, ionized in the SOL/plasma edge, will be susceptible to be transported onto the first wall, increasing in this way the associated lithium and concomitant fuel deposition. Although a thorough analysis of these erosion/redeposition phenomena is out of the scope of the paper, it is interesting to comment how they can affect to the presented results.

General impurity transport considerations [45] establish that if $\lambda_{\text{Li}}^{+} < r_{L}^{' 2}$, (where $\lambda_{\text{Li}}^{+}$ is the lithium ionization length and $r_{L}^{'}$ the Li Larmor radius) the Li+ ions will prompt re-deposited on the divertor surfaces. As first case we will estimate these values for the case of thermal (evaporated at 450 °C) Li atoms. Lithium ionization length can be estimated as:

$$\lambda_{\text{Li}}^{+} = \nu_{\text{Li}}^{+} (\langle \sigma \nu \rangle n_e)^{-1}, \quad (8)$$

where $\nu_{\text{Li}}^{+}$ is the thermal velocity of Li ions, considered at the temperature limit of 450 °C, $\langle \sigma \nu \rangle$ is the rate coefficient for the 1st electron impact ionization of the Li atoms (that depends on $T_e$), and $n_e$ the electron density. Assuming the conservative DEMO divertor values for $n_e$ and $T_e$ of $2 \cdot 10^{20} \text{m}^{-3}$ and 1.5 eV respectively, we obtain values of $\langle \sigma \nu \rangle = 1.25 \times 10^{-8} \text{cm}^3 \text{s}^{-1}$ and finally $\lambda_{\text{Li}}^{+} = 6.4 \cdot 10^{-2} \text{cm}$. The Larmor radius can be calculated using this expression [46]:

$$\rho_{L}^{'} = 102 (\mu \cdot T_e)^{1/2} (Z \cdot B)^{-1} (\text{cm}), \quad (9)$$

where $\mu$ is the ratio between the Li+ ion mass and the proton mass ($m_{\text{H}}/m_{\text{D}}$), $Z$ is the charge state (+1), $T_e$ the ion temperature (eV) and B the magnetic field in Gauss units (G). Using for $T_e$ the value of thermal temperature of the evaporated Li atoms and $B = 6 \text{T}$ (equivalent to 60000 G), we obtain $\rho_{L}^{'} = 10^{-3} \text{cm}$, a value that does not match the general prompt re-deposition criterion.

For the case of neutral Li sputtered atoms, they will be ejected from the Li surface with a minimum energy content equal to the Li binding energy [47] (1.68 eV) that would determine a conservative value for its velocity. Using this value and the same values for $n_e$, $\langle \sigma \nu \rangle$ and $T_e$, by applying the equation (8) a value of $\lambda_{\text{Li}}^{+} = 0.34 \text{cm}$ is obtained. Considering $T_e$ equals to the Li binding energy and $B = 60000 \text{ G}$ the equation (9) gives a value of $\rho_{L}^{'} = 6 \cdot 10^{-3} \text{cm}$. With these numbers and the assumed criterion, even for the most favorable case (minimum energy for sputtered atoms and minimum value for $\lambda_{\text{Li}}^{+}$), values of $\lambda_{\text{Li}}^{+} > \rho_{L}^{'}$ are obtained. These numbers indicate that for conservative DEMO divertor conditions, prompt re-deposition of these evaporated and sputtered Li impurities is not likely happening. Consequently, the possible lack of local re-deposition must be taken into account for the integration of our findings in a real reactor scenario, being a modelling/simulation approach under DEMO divertor conditions completely necessary.

Secondly, exploring the predictions about the distribution of the pressure levels inside the DEMO vacuum vessel [48, 49], the molecular D$_2$ pressure value used in our Li–D$_2$ deposition regime experiments (0.67 Pa) is comparable to the expected pressures in zones close to the separatrix and SOL region. However, in the sub-divertor areas around this region, the neutral pressure decreases strongly with pressures around 0.01 Pa [48]. In the W first wall areas situated at a larger distance from the divertor region or plasma shadowed, the neutral pressure is expected to be even lower, ultimately given by the recycling properties of the material. On them, the obtained results seem representative and could be, in principle, taken into account as reasonable Li and D retention estimations. However, it is important to note that in the global first wall, the associated larger charge-exchange (CX) and sputtering neutral fluxes may dominate the co-deposition instead the pressure.
For the global reactor first wall environment, the thermal Li and D₂ deposition scenario is not the most realistic scenario, as during the D–T reactor operation the W first wall surface would be affected by simultaneous Li and D (neutral, molecular and ionic) incident fluxes, as well as by an intense bombardment with energetic neutrons and helium ions. The influence of fuel ionic bombardment in the retention on hybrid W–Li films is expected to be quite important as the magnitude of the ionic flux, especially on first wall zones close to the divertor, will be very considerable. This ionic bombardment will produce the implantation of Li and fuel species that will affect the tritium inventory. About this issue, it should be pointed out that previous experiments with cold \((T_{\text{surface}} \approx 400 \, ^\circ\text{C})\) W samples exposed to Li-seeded H₂ glow discharge (GD) plasmas [14] found a lower hydrogen retention compared to pre-lithiated W samples later exposed to H₂ GD plasmas, suggesting that no extra hydrogenic retention will be produced by the lithium implantation in comparison to the expected on lithium simply deposited. Additionally, very promising results have been obtained in terms of fuel retention and Li film formation for hot W samples exposed to Li-seeded deuterium linear plasmas in the PISCES-A divertor simulator [50]. These results presented in the worst case a retention (atomic ratio) at \(T_{\text{surface}} = 400 \, ^\circ\text{C}\) higher by two orders of magnitude compared with the retention found for our sample WLd10 prepared at the same surface temperature. Despite these encouraging results, in order to have a global vision of the W–Li mixing processes, and its associated fuel retention problems expected in a reactor with the proposed PFM scenario, the fuel retention on the reactor first wall areas affected by Li deposition/implantation together with intense plasma, neutron and CX bombardment during longer time scales must be wider studied.

5. Conclusions

The presented results show a non-linear effect of the surface temperature in the deuterium retention found on thin liquid Li films pre-deposited on hot W, being this result probably related with a different pattern for the thermodynamic interaction of the thin liquid Li films with deuterium compared to the traditional case of liquid bulk absorption. Additionally, even at \(T_{\text{surface}} = 225 \, ^\circ\text{C}\), the W sample exposed to simultaneous thermal deposition of Li and D₂ showed the formation of a lithium film \(\approx 2 \, \mu\text{m}\) thick while the associated deuterium retention was below the sensibility of the LID technique, showing a similar behaviour compared to pure W.

Although other aspects related with the presence of high ionic/recombination fuel, neutron fluxes and the associated harmful effects in the fuel retention have not been approached, these results represent a first approximation to the problematic of the potential formation of thick Li–D co-deposits on especially problematic in-vessel reactor areas (remote from plasma and/or plasma shadowed) that could accumulate uncontrolled amounts of tritium.

The exhaustive experimental work points to that the operation with a hot W first wall \((T = 400 \, ^\circ\text{C})\) would be associated to the formation of thin liquid Li films (thickness of few microns) whose associated fuel retention (in the case of only thermal molecular species) would result extremely low, at the same level compared to the retention in pure W elements (atomic D/Li ratio <0.1 at.%). This attractive result supposes an encouraging perspective in terms of retention and precluding of hydride formation on the W–Li films situated on remote or plasma shadowed areas of the W first wall that could threaten the operation of a reactor combining both PFM systems due to the associated risks related with the allowed tritium administrative limits. However, it is important to note that even in future reactors, the use of a hot W first wall \(T \geq 400 \, ^\circ\text{C}\) might not be assured due to economical or engineering limitations. Additionally, several diagnostics and/or heating systems could need lower working temperatures.

For the extrapolation of these findings to the global tritium retention problematic of a DEMO-like reactor, the promising experimental results must be confirmed in experimental conditions that would include ionic/neutral and molecular Li/D fluxes to determine if this low D saturation regime found in the W–Li films can be achieved in a reactor-like regime. The possibility of exposing tungsten to Li–D₂ co-deposition environments in the recently upgraded Magnum-PSI linear device, that will enable a material exposure under experimental conditions characterized by extremely large plasma fluences and longer term exposures closer to a reactor scenario, appears very attractive for this purpose.

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