

# Influence of H<sub>2</sub> and D<sub>2</sub> plasmas on the work function of caesiated materials

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Caesium covered surfaces are used in negative hydrogen ion sources as low work function converter for H<sup>-</sup>/D<sup>-</sup> surface production. The work function  $\chi$  of the converter surface is one of the key parameters determining the performance of the ion source. Under idealized conditions pure bulk Cs has 2.14 eV. However, residual gases at ion source background pressures of 10<sup>-7</sup>–10<sup>-6</sup> mbar and plasma surface interaction with the hydrogen discharge in front of the caesiated surface dynamically affect the actual surface work function. Necessary fundamental investigations on the resulting  $\chi$  are performed at a dedicated laboratory experiment. Under the vacuum conditions of ion sources, incorporation of impurities into the Cs layer leads to very stable Cs compounds. The result is a minimal work function of  $\chi_{\text{vac}} \approx 2.75$  eV for Cs evaporation rates of up to 10 mg/h independent of substrate material and surface temperature (up to 260 °C). Moreover, a distinct degradation behavior can be observed in absence of a Cs flux onto the surface leading to a deterioration of the work function by about 0.1 eV/h. However, in a hydrogen discharge with plasma parameters close to those of ion sources, fluxes of reactive hydrogen species and VUV photons impact on the surface which reduces the work function of the caesiated substrate down to about 2.6 eV even without Cs supply. Establishing a Cs flux onto the surface with  $\Gamma_{\text{Cs}} \approx 10^{17} \text{ m}^{-2}\text{s}^{-1}$  further enhances the work function obtaining values around 2.1 eV, which can be maintained stable for several hours of plasma exposure. Hence, Cs layers with work functions close to that of pure bulk Cs can be achieved for both H<sub>2</sub> and D<sub>2</sub> plasmas. Isotopic differences can be neglected within the measurement accuracy of about 0.1 eV due to comparable plasma parameters. Furthermore, after shutting down the Cs evaporation continuing plasma exposure helps against degradation of the Cs layer resulting in a constant low work function for at least one hour.

## I. INTRODUCTION

Negative hydrogen and deuterium ion sources<sup>1</sup> are applied for front-ends of particle accelerators and for neutral beam injection systems of future fusion devices like ITER. In such sources, negative hydrogen ions are predominantly produced via the surface conversion mechanism: particles from a low pressure low temperature hydrogen or deuterium discharge are converted to negative ions by picking up one or more electrons from a converter surface. The efficiency of this process significantly depends on the work function  $\chi$  of the surface. For this purpose the converter is covered with the alkali metal caesium which lowers its surface work function and thus significantly increases the negative ion yield<sup>1, 2</sup>. Hence, quantification of the work function and identification of its influencing factors are mandatory for optimization of negative ion sources; especially in view of the powerful large-scale negative ion sources required for the next generation of fusion devices like ITER, where negative ion beams of several ten amperes have to be generated homogeneously over an area of several m<sup>2</sup> and stable for several thousand seconds.

Quantified values for the reduction of  $\chi$  for substrates covered with fractional Cs layers can be found in various publications for ultra-high vacuum conditions (background pressure below 10<sup>-9</sup> mbar) depending on the substrate material and its crystallographic orientation at the

surface<sup>3–5</sup>. Independent of the actual substrate a comprehensive trend can be observed: for Cs coverages below 0.5 monolayers  $\chi$  decreases until at about 0.5–0.7 monolayers a minimum is obtained achieving an electron work function of about 1.5–1.7 eV. For covering fractions of a full monolayer and above the bulk value of a pure Cs surface of 2.14 eV<sup>6</sup> is attained.

The work function behavior described above was obtained under "ideal" conditions without plasma and only negligible contamination by background gases. On the other hand, in ion sources the background pressure is typically in the range of 10<sup>-7</sup>–10<sup>-6</sup> mbar. Furthermore, plasma discharges in H<sub>2</sub> or D<sub>2</sub> are repetitively generated with a certain duty cycle. In the case of ion sources applied for neutral beam injection in fusion research, the electron temperature, electron and positive ion densities and atomic hydrogen densities of the plasmas are in the range of 1–2 eV, 10<sup>16</sup>–10<sup>17</sup> m<sup>-3</sup> and 10<sup>19</sup> m<sup>-3</sup>, respectively. For ion sources applied for particle accelerators these values are even higher by about an order of magnitude each. In this case, the Cs layer and thus its work function is affected by the formation of Cs compounds on the converter surface due to the presence of a non-negligible amount of residual gases. These compounds degrade the work function by their non-metallic nature. On the other hand, the low temperature hydrogen plasma causes a flux of reactive plasma species (atomic hydrogen H and positive hydrogen ions H<sub>x</sub><sup>+</sup>) and VUV/UV radiation onto the surface. The interaction of these fluxes with the caesiated surface leads to a variety of processes, including – but not limited to – adsorption of hydrogen par-

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ticles, chemical reactions as well as chemical, thermal and photon-induced desorption of contaminants and/or caesium from the surface, where the synergistic effect on the work function is not easily anticipated. Due to this multitude of influences, values of measurements performed at ultra-high vacuum conditions cannot be applied directly to ion sources and dedicated studies have to be performed.

Some measurements of the work function of the converter surface in caesiated negative ion sources exist<sup>7–11</sup>. These studies rely on measuring the photocurrent emerging from photon impact onto the converter surface using Fowler's theory for determination of the work function<sup>12</sup>, where mostly only a single photon frequency is used. However, the actual photocurrent depends not only on the work function but on more parameters, like the Fermi energy for instance<sup>12,13</sup>. This effect can only be accounted for by using several different photon energies together with an appropriate evaluation procedure and a thorough calibration directly at the actual setup used for the measurements<sup>13</sup>. This approach is, however, not easily viable at the high power ion sources, why dedicated flexible small-scale experiments are preferred.

Hence, fundamental investigations on the work function of caesiated surfaces under ion source conditions in vacuum and plasma are carried out at the laboratory experiment ACCesS<sup>14,15</sup>. The setup allows to determine reliable absolute values for the work function of sample surfaces depending on a variety of quantifiable parameters, like Cs flux or the surface temperature. First measurements on the work function of caesiated surfaces upon plasma exposure have already been shown in Gutser et al.<sup>16</sup>. In this paper these studies are extended using both pure H<sub>2</sub> and D<sub>2</sub> discharges and a reliable and finely adjustable Cs source. Furthermore, the measurements are monitored by a comprehensive set of diagnostics, applicable simultaneously to the work function measurements.

## II. EXPERIMENTAL SETUP

The laboratory experiment ACCesS (Augsburg Comprehensive Cesium Setup)<sup>14,15</sup> consists of a stainless steel vessel with 15 cm in diameter and 10 cm in height. Background pressures of 10<sup>-6</sup> mbar are obtained by a turbomolecular pump. Plasmas are generated via inductive RF coupling (frequency 27.12 MHz, max. 600 W RF power) using a planar coil located on top of the vessel. The setup has a manifold of ports allowing for the attachment of a variety of peripheral equipments and diagnostics. In order to assure stable temperature conditions, which is of particular interest for the highly dynamic redistribution processes of the Cs content, the vessel walls are temperature controlled via the cooling water circuit of the discharge vessel. During the presented campaigns the temperature was kept below 30 °C. Cs seeding is done by evaporation from a finely adjustable Cs dispenser oven<sup>17</sup>

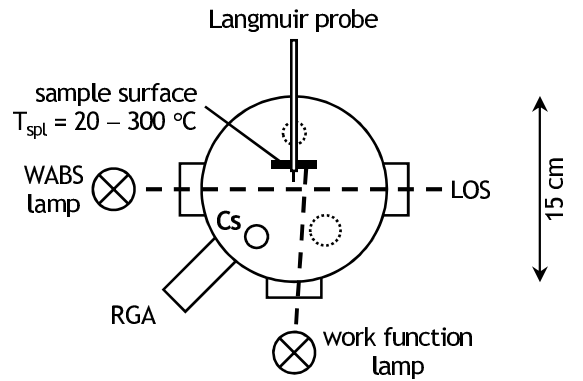


FIG. 1. Top view of the experimental setup including the arrangement of the diagnostics and the sample surface.

placed at the bottom plate. Near the center of the vessel a sample holder is mounted, electrically and thermally insulated from the grounded vessel walls. Samples of the size of 3 × 3 cm<sup>2</sup> can be heated PID controlled up to 300 °C. Owing to the insulated mounting of the sample holder the temperature of other components within the vessel, especially of the vessel wall, remains unaffected.

The arrangement of the diagnostics is shown in figure 1: the Cs evaporation rate is measured via a surface ionization detector (SID) mounted at the oven nozzle<sup>17</sup> (denoted with 'Cs' in the figure), the volume averaged Cs density is determined by means of white light absorption spectroscopy (WABS) via the diagonal line-of-sight (LOS), the impurity content is monitored by a residual gas analyzer (RGA) and the work function is determined via the photoelectrical effect using the highly intense UV emission from a high pressure mercury lamp (100 W). In plasma operation, a Langmuir probe located at the center of the vessel is used to determine the local electron density, the electron energy distribution function (EEDF) as well as the plasma potential. Optical emission spectroscopy (OES) via the diagonal LOS is applied for determining the following volume averaged plasma parameters: atomic hydrogen or deuterium density, gas temperature, vibrational temperature of the hydrogen or deuterium molecule in the ground state and the electron temperature. Details on the applied diagnostics in plasma operation can be found in another publication<sup>14</sup>.

Determination of the work function  $\chi$  of the sample surface is described in detail in a preceding paper<sup>13</sup> and is only briefly recapitulated here. The radiation from the UV lamp is focused onto the sample which is biased negatively with respect to the vessel walls ( $\sim 30$  V). The resulting photocurrent is measured by a Keithley 602 Electrometer. Several different photon energies are selected via interference filters mounted at the mercury lamp. The resulting photocurrent depends on the energy of the incident photons, the work function of the surface as well as its temperature. Using Fowler's theory<sup>12</sup> a value for  $\chi$  can be evaluated, where the wavelength depending intensity of the incident photons needs to be

accounted for. This is done by a thorough calibration of the entire setup using an absolutely calibrated spectrometer. However, as pointed out recently<sup>13</sup>,  $\chi$  values determined after the Fowler method are always an upper limit for the actual work function. Thus, a correction procedure<sup>13</sup> is applied to each determined value. In this way, absolutely quantified work functions can be evaluated with high accuracy.

Due to the bias voltage, measurements cannot be performed during plasma operation, since the actual photocurrent would be superimposed by a much higher current coming from the plasma electrons. Thus, the influence of plasma surface interaction on the work function is approached by pulsed plasma operation, where  $\chi$  is determined during the plasma-off phases. In Gutser et al.<sup>16</sup> an elaborate setup is presented using a continuously pulsed plasma with a frequency of 18.5 Hz. In order to assure plasma ignition for each pulse a 20% admixture of helium to the hydrogen discharge was required. However, in Kolesnychenko et al.<sup>18</sup> it is shown that adsorption of helium on a surface might lead to the determination of increased work function values. Thus, in order to eliminate any possible adverse effects of a helium admixture, pure hydrogen and deuterium discharges are used in the present paper. A pulsed mode with high frequency is, however, not possible for pure hydrogen plasmas and thus, the plasma is manually switched off and on consecutively. Measuring the energy dependent photocurrents for a single value of  $\chi$  takes about three minutes. Hence, continuous plasma operation of several minutes (up to hours) is intermitted by plasma-off phases of about three minutes in which the work function is determined.

### III. WORK FUNCTION MEASUREMENTS

In order to obtain stable conditions within the experimental setup about 1 mg of Cs is evaporated into the system prior to the measurements presented here. The behavior of the experiment during this conditioning process can be found in a preceding publication<sup>19</sup> showing the typical impact due to the getter effect of caesium: decreasing background pressure and residual gas contents. Hence, the following results were obtained at an experiment in equilibrium, i. e. the vessel walls are already covered with caesium (except for the campaign of the "second case" in fig. 2) and the background pressure as well as the residual gas contents are stable. Furthermore, the presented measurements are started only after thermal equilibrium of the entire experiment. The background pressure is around  $10^{-6}$  mbar and – despite the effect of caesium evaporation – the composition of the residual gases is typical for vacuum chambers which are not baked out, i. e. water vapor  $H_2O$  is still the dominant residual gas with 80–90%, followed by nitrogen  $N_2$  and/or carbon monoxide  $CO$  with 10–20% (both have mass 28). The base pressure and its composition are equivalent to the conditions at the ITER prototype ion source<sup>20</sup> at

the Max-Planck-Institut für Plasmaphysik (IPP). In this state of the experiment, further evaporation of caesium into the system has only negligible influence on the vacuum conditions and the resulting measurements can be related to the pure effect of caesium adsorption on the sample surface.

#### A. Caesiation in vacuum and temperature dependence

The influence of an increasing Cs evaporation rate on the work function of a stainless steel sample under these vacuum conditions is presented in a preceding publication<sup>13</sup>. Adsorption of Cs on the surface thus leads to a continuous decrease of the work function, where a saturation value is reached above a Cs evaporation rate of around 1.5 mg/h: the lowest possible value is determined to be  $\chi_{vac,steel} \approx 2.75$  eV in contrast to  $\chi_{Cs,bulk} = 2.14$  eV for pure bulk Cs layers. Hence, the non-negligible amount of impurities from the residual background gases leads to an increased work function compared to caesiation under ultra-high vacuum conditions. Furthermore, the Cs layer on the substrate can be expected to be thick: At 1.5 mg/h evaporation rate the Cs density above the surface is  $n_{Cs} \approx 2 \times 10^{15} m^{-3}$  which leads to a Cs flux onto the surface of  $\Gamma_{Cs} \approx 1.5 \times 10^{17} m^{-2}s^{-1}$ . Together with an expectable high sticking probability for Cs on the substrate<sup>21</sup>, this flux translates to a layer growth of about 50 layers per hour. On the other hand, the flux of residual gases onto the surface at a background pressure of  $10^{-6}$  mbar is around  $3 \times 10^{18} m^{-2}s^{-1}$ , which illustrates their significance in Cs adsorption dynamics. The impact of contaminant adsorption can also be observed when the Cs evaporation is shut down: the work function starts to increase with a rate of about +0.1 eV/h due to the degradation of the surface layer by incorporation of impurities. The degradation rate decreases with time such that after some days in vacuum work function values of up to 3.3 eV can be reached.

The impact of impurities on the Cs layer should be affected by the surface temperature since it determines the equilibrium between adsorption and desorption and thus the resulting impurity coverage on the surface. Thus, the stainless steel sample was furthermore actively heated and the influence on the work function was investigated<sup>22</sup>. The results are shown in figure 2, where two different campaigns are considered: heating an already caesiated sample and caesiating a bare sample at elevated surface temperatures.

For the first case, a caesiated stainless steel sample is left in vacuum for some days resulting in a degraded work function of slightly above 3 eV. Without supplying additional Cs, the sample is heated in several steps: 100–150–200 °C. Each time the temperature is raised a sudden but temporary increase of the background pressure accompanied by a Cs flux emerging from the surface (detected by the SID at the oven) is observed<sup>19</sup>. The influence of desorption of adsorbates on the work function

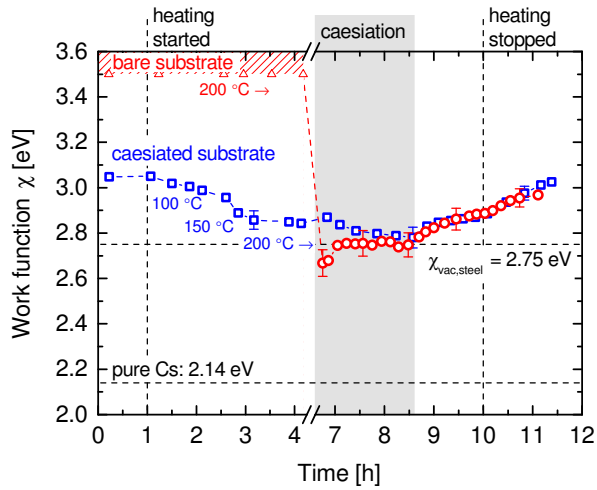


FIG. 2. Influence of elevated temperatures on the work function of caesiated stainless steel samples, starting from a bare sample surface and from an already caesiated one.

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is shown in figure 2 in blue squares: The result is a purification of the surface layer by which the work function decreases down to around 2.8 eV. Setting in Cs evaporation with a rate of around 1.6 mg/h further decreases the work function down to the saturation level of  $\chi_{\text{vac,steel}}$ .

In the second case (red circles), a fresh stainless steel sample was introduced into the experiment and heated to 200 °C. Heating is accompanied by a temporarily increasing background pressure, whereas the signal from the SID (Cs flux) remains unaffected. This is attributed to thermal desorption of contaminants and thus, a diminished amount of adsorbed impurities on the sample surface is expected. The high surface temperature is maintained during the following caesiation process, which is moreover accompanied by a steady decrease of the background pressure by about a factor of three owing to the gettering effect of caesium. In fact, a work function of 2.7 eV is obtained directly after onset of Cs evaporation ( $\approx 1.9$  mg/h), which is ascribed to the expected purified substrate. However, also in this case the saturated work function level of the caesiated stainless steel sample is again at 2.75 eV, even for evaporation rates up to 5.5 mg/h. After shutting down the Cs evaporation it can be seen for both cases, that with elevated surface temperatures the degradation seems to slow down at work function values of around 2.9 eV. Only after stopping the active heating the work function quickly degrades to values of 3 eV and above.

So far, investigations were performed using stainless steel as substrate material in order to avoid different material types within the stainless steel setup. The converter surface in negative ion sources is, however, made from molybdenum and thus, first investigations regarding a possible influence of the substrate material were

performed. Caesiating a molybdenum sample in an ion source relevant vacuum shows, however, a very similar behavior to the observations with stainless steel: a minimal work function value of about 2.7 eV could be attained and also the degradation progression shows little difference. These observations corroborate the statement that the behavior of caesiated surfaces under ion source vacuum conditions is determined by the interplay of the adsorbed caesium with the influx of impurities from the background gas. Thus, the actual substrate material is subordinate, since effects would only be observable with a pure substrate surface covered with a sub-monolayer of pure caesium.

In further campaigns also temperatures of up to 260 °C and/or evaporation rates of up to 10 mg/h were tested, in line with typical values at negative ion sources. Nevertheless, in all the cases the lowest possible value was  $\chi_{\text{vac}} \approx 2.75 \pm 0.1$  eV. To obtain and maintain this value, evaporation rates above 1.5 mg/h are sufficient, correlated to a Cs flux onto the substrate of some  $10^{17} \text{ m}^{-2} \text{ s}^{-1}$ . The determined  $\chi$  values are also summarized in table I. The saturation of the work function indicates, that the flux of impurities from the residual gas leads to very stable compounds whose influence on the surface work function cannot be compensated under ion source relevant vacuum conditions.

## B. Influence of plasma exposure

The impact of plasma surface interaction on the work function of caesiated surfaces is studied for both  $\text{H}_2$  and  $\text{D}_2$  at 10 Pa gas pressure and 250 W RF power, where ion source relevant plasma parameters are present<sup>15</sup>:  $T_{e,\text{H}_2} \approx T_{e,\text{D}_2} \approx 2$  eV,  $n_{e,\text{H}_2} \approx n_{e,\text{D}_2} \approx 4 \times 10^{16} \text{ m}^{-3}$ ,  $n_{\text{H}} \approx 1 - 2 \times 10^{19} \text{ m}^{-3}$  and  $n_{\text{D}} \approx 2 - 2.5 \times 10^{19} \text{ m}^{-3}$ . Plasma exposure is intermitted every 10 to 20 min. in order to measure the work function (gas phases of 3–5 min.). Figure 3 shows the influence of  $\text{H}_2$  plasma exposure on the work function of a stainless steel sample which was caesiated in vacuum before and left in a  $10^{-6}$  mbar vacuum for some days. The degraded Cs layer shows a work function of slightly above 3 eV at the beginning.

Starting the plasma (without Cs evaporation at first) directly leads to a drop of the work function below the minimally achieved value in vacuum. The longer the surface is subject to plasma exposure the further decreases its work function. After about 3 hours a value of 2.5–2.6 eV is reached. Afterwards Cs evaporation is started obtaining Cs densities within the plasma volume of  $1 - 4 \times 10^{15} \text{ m}^{-3}$ . The flux of Cs onto the surface with in average  $\Gamma_{\text{Cs}} \approx 1.5 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1}$  quickly leads to a further decrease of the work function down to  $2.2 \pm 0.1$  eV. For almost three hours the work function is more or less stable at 2.2–2.3 eV. Furthermore, shutting down the Cs evaporation has virtually no effect on the surface work function and the low  $\chi$  values are maintained in the  $\text{H}_2$  plasma for at least one hour. However, switching off the

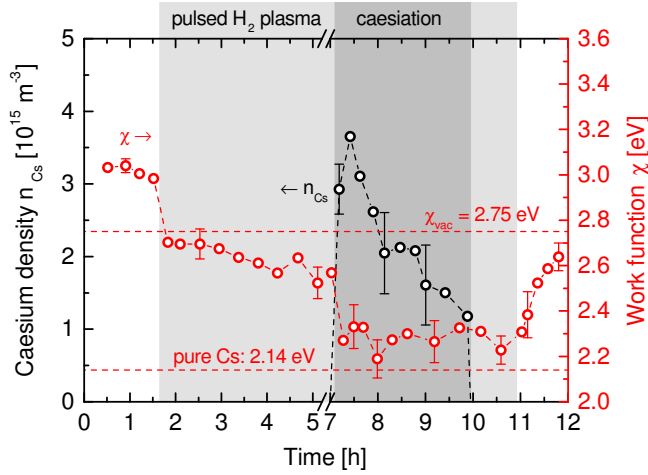


FIG. 3. Work function of a caesiated stainless steel sample during  $\text{H}_2$  plasma exposure (10 Pa, 250 W) with and without additional Cs evaporation. Work function measurements are performed every 10 to 20 min. in short intermediate gas phases.

plasma directly leads to a quick deterioration of the work function.

Figure 4 shows the comparison of an equivalent campaign in deuterium starting again with a degraded Cs layer on stainless steel. It can be seen, that for the deuterium plasma (again in absence of Cs evaporation at first) it takes longer to reach work function values below the minimal vacuum level. Only after about 3 hours of deuterium plasma exposure, work function values comparable to the  $\text{H}_2$  case can be reached, taking into account the measurement uncertainty. Introducing Cs evaporation ( $n_{\text{Cs}} \approx 0.5 - 2 \times 10^{15} \text{ m}^{-3}$ ) steadily decreases the surface work function and values around  $2.0 \pm 0.2 \text{ eV}$  are obtained.  $\chi$  values of 2.0–2.2 eV can be maintained in the  $\text{D}_2$  plasma for about three hours and again only a slight effect of shutting down the Cs evaporation can be seen. Again, degradation upon switching off the discharge directly leads to a steep increase of the work function.

### C. Discussion

The obtained work function values for the performed campaigns on caesiated materials are summarized in table I. It was shown, that in an ion source relevant vacuum of  $10^{-6} \text{ mbar}$  (80–90% water vapor) the minimally achievable work function of a Cs layer is  $\chi_{\text{vac}} \approx 2.75 \text{ eV}$  independent of substrate material or surface temperature. The reason is expected to be the influx of residual gases onto the surface leading to incorporation of impurities into the Cs layer where stable Cs compounds with binding energies of up to  $12 \text{ eV}^{23}$  can be formed. Exposing such a caesiated surface to a hydrogen plasma can decrease the work function below  $\chi_{\text{vac}}$  even if no additional Cs flux onto the surface is present. After some hours of

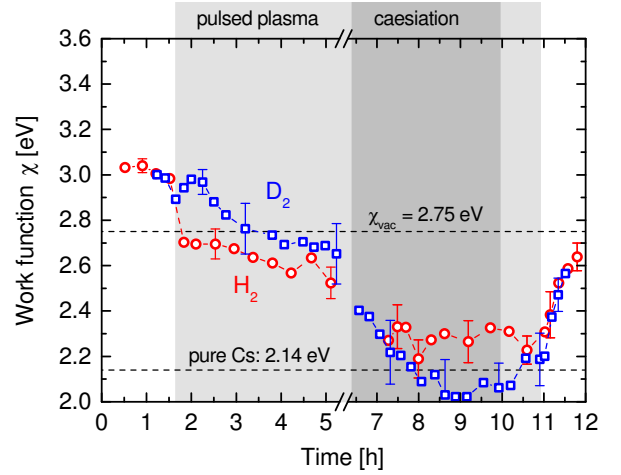


FIG. 4. Influence of  $\text{H}_2$  and  $\text{D}_2$  plasmas (10 Pa, 250 W RF power) on the work function of a caesiated stainless steel surface before, during and after caesiation. Work function measurements are performed every 10 to 20 min. in short intermediate gas phases.

plasma exposure  $\text{H}_2$  and  $\text{D}_2$  discharges lead to comparable  $\chi$  values which are, however, still about 0.4 eV higher than for pure bulk Cs. Only together with a flux of fresh Cs onto the surface, coatings can be achieved resembling a work function of pure Cs layers.

For an explanation of the observed behavior in-situ diagnostics for the surface characteristics would be preferable which, however, are not available at ACCesS. Moreover, due to the hygroscopic characteristic of Cs and Cs compounds ex-situ measurements cannot be related to the actual situation in vacuum or during plasma. However, particle and photon fluxes involved in plasma surface interaction can be considered.

The surface temperature during plasma exposure reaches  $250^\circ \text{C}$  in maximum, which is also the maximal temperature applied in vacuum showing no effect on the achievable work function. Hence, the plasma effect cannot be explained by the high surface temperature only, but it may play a role for synergistic effects. In plasma, reactive hydrogen species as well as photons in the UV and VUV spectral range impinge upon the surface. The potential of the floating surface is measured to be around 8 V below the potential of the plasma close to the surface for both  $\text{H}_2$  and  $\text{D}_2$  plasmas, which leads to ion fluxes impacting the surface with energies of  $\approx 8 \text{ eV}$  in maximum for both cases (assuming a collisionless sheath). Using the given plasma parameters<sup>15</sup>, atomic fluxes of  $\Gamma_{\text{H}} \approx \Gamma_{\text{D}} \approx 10^{22} \text{ m}^{-2} \text{ s}^{-1}$  and Bohm fluxes of  $\Gamma_{\text{H,ion}} \approx 9 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}$  and  $\Gamma_{\text{D,ion}} \approx 6 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}$  are calculated. Furthermore, radiation of a hydrogen or deuterium plasma has photon energies of up to 15 eV with VUV fluxes of the same order of magnitude as occurring ion fluxes (see e.g. Fantz et al.<sup>24</sup> for a detailed discussion on occurring VUV spectra and fluxes in  $\text{H}_2$  plasmas). Both these particle and photon energies are

TABLE I. Minimally achieved work function values throughout the measurement campaigns for several surface materials as well as conditions, like being heated or degraded (" $> 4.3$ " means higher than absolutely determinable with this setup). Given error ranges only represent the error of the evaluation of that specific measurement. Another  $\pm 0.1$  eV may be added regarding the reproducibility of the specific surface condition and the issues explained in Friedl<sup>13</sup>.

Initial surface condition	Work function $\chi$ [eV]		Reference
	without Cs evaporation	with Cs evaporation ( $\sim$ mg/h)	
bare stainless steel	$> 4.3$	$2.77 \pm 0.06$	Friedl <sup>13</sup>
degraded Cs layer	$\sim 3.0 - 3.3$	$2.75 \pm 0.07$	Friedl <sup>13</sup>
heated degraded Cs layer	$2.84 \pm 0.04$	$2.78 \pm 0.05$	Friedl et al. <sup>22</sup>
heated stainless steel	$> 4.3$	$2.74 \pm 0.06$	Friedl et al. <sup>22</sup>
bare molybdenum	$> 4.3$	$2.69 \pm 0.05$	this paper
degraded Cs layer in H <sub>2</sub> plasma	$2.52 \pm 0.07$	$2.19 \pm 0.08$	this paper
degraded Cs layer in D <sub>2</sub> plasma	$2.65 \pm 0.13$	$2.03 \pm 0.16$	this paper
pure bulk Cs	–	2.14	Michaelson <sup>6</sup>

sufficient to break bondings of chemical Cs compounds (4.3 eV for CsOH for instance<sup>23</sup>) and moreover exceed the adsorption enthalpies of the contaminants (e.g. around 1 eV for H<sub>2</sub>O on stainless steel<sup>25</sup>). The synergistic influence of particle and photon fluxes is thus expected to cause desorption of impurities from the surface. Hence, the decrease of the surface work function due to plasma exposure (without Cs supply to the sample surface) is explained by a decreasing amount of chemically bound Cs on the surface. If furthermore Cs is evaporated, a flux of Cs as well as Cs ions onto the surface is established while the plasma parameters are not affected<sup>15</sup>. In particular Cs ions can have a much stronger impact on the Cs layer than hydrogen particles due to their much higher mass (though their flux is several orders of magnitude smaller due to the small density and high mass). Hence, strong indications are given for an effective surface cleaning and replenishing by the occurring hydrogen and caesium particle and photon fluxes. The result is a surface coating with work function values around those of a virtually pure Cs layer.

At the occurring ion energies of several electron volts, physical sputtering by hydrogen particles is negligible compared to chemical effects and thus, the isotopic mass difference between hydrogen and deuterium particles is only relevant for the absolute ion fluxes:  $\Gamma_{D,ion} = \Gamma_{H,ion}/\sqrt{2}$ . Other plasma parameters of H<sub>2</sub> and D<sub>2</sub> discharges at ACCesS including ionic energies and atomic fluxes are, however, comparable<sup>15</sup>. Hence, a slightly reduced impact of D<sub>2</sub> plasmas is expected due to the ion fluxes which might explain the differing reaction of the work function directly after onset of plasma exposure compared to H<sub>2</sub>. However, for the rest of the campaign isotopic differences in  $\chi$  are determined to be below the measurement accuracy. This shows, that there is no fundamental difference between hydrogen and deuterium exposed caesiated surfaces and only the corresponding plasma parameters are decisive.

The low  $\chi$  values can be maintained in plasma also when Cs evaporation is switched off (interval between

10 h and 11 h in the figures). Hence, in contrast to the observations in vacuum, the hydrogen plasma seems to counteract a degradation of the Cs layer preserving the low work function surface. However, the energy of impinging particles and photons also exceeds the binding energy of Cs at the surface (up to 3.4 eV for sub-monolayer coatings<sup>26</sup>). Hence, hydrogen plasma exposure of a caesiated surface can also remove Cs from the surface. This removal needs to be counteracted by an influx of caesium, where a lower limit for the absolute flux  $\Gamma_{Cs}$  is expected below which long-time exposure by a hydrogen plasma leads to a reduction of the Cs coverage on the surface and thus to an increasing work function again. This effect was recently confirmed experimentally<sup>27</sup>: within 4 hours of hydrogen plasma exposure without Cs supply, work functions of up to 3.7 eV and above are obtained. The presented results in figures 3 and 4 show already, that at least a Cs flux of around  $10^{17} \text{ m}^{-2} \text{ s}^{-1}$  is sufficient to maintain a stable work function during continuous hydrogen plasma exposure.

However, switching off the RF (at 11 h in the figures) directly leads to a deterioration of the Cs layer with rates of more than  $+0.4 \text{ eV/h}$ . This degradation rate is about a factor of four higher than for the vacuum case ( $+0.1 \text{ eV/h}$ ), which can be explained by the expected higher share of areas with pure Cs on the surface where the chemical reactivity should be higher than at areas with already reacted Cs. It can be anticipated that the degradation rate will decrease once the work function surpasses the value of  $\chi_{vac}$ .

Summarizing, it can be stated that in ion source relevant hydrogen discharges Cs layers close to pure bulk Cs can be obtained and that in absence of a Cs flux onto the surface, plasma exposure is furthermore beneficial for cleaning and against degradation of the Cs layer. However, a certain Cs flux onto the surface is required in order to maintain a stable work function for long-time plasma exposure.

Still it has to be mentioned, that the impact of plasma surface interaction is mainly determined by the flux and

the energy of the impinging ions and VUV photons, where the ion energy for instance is mainly determined by the potential difference between the bulk plasma and the converter surface. At ion sources, this value is typically in the range of several volts<sup>1</sup>, which is the same range as in the present investigations. However, at ion sources the converter surface might be biased with varying voltages throughout operation, including changing polarity (or even with self-adjusting voltages, when the bias current is set). Consequently, in a next step, the influence of applying different bias voltages to the sample surface will be investigated at ACCeS.

#### IV. CONCLUSION

The work function of the caesiated converter surface is a main parameter determining the performance of negative hydrogen ion sources. Values for caesiated materials found in the literature can, however, not be applied due to the non-negligible amount of impurities under ion source background pressures and the recurring plasma exposure. Hence, fundamental investigations aiming at identification of parameters determining the work function of Cs layers under ion source conditions have to be performed at dedicated experiments.

It was shown that under ion source relevant vacuum conditions the flux of caesium onto the surface is still the decisive parameter for its work function. However, under the dominant influx of residual gases (mainly water vapor) lowering of the work function saturates above a Cs flux of some  $10^{17} \text{ m}^{-2} \text{ s}^{-1}$  and the minimally achievable value is reached:  $\chi_{\text{vac}} \approx 2.75 \text{ eV}$ . Neither high surface temperatures nor higher Cs fluxes help to further decrease this value. However, particle and photon fluxes from a low pressure low temperature hydrogen plasma with flux energies in the range of several electron volts can cause desorption of contaminants from the Cs layer. Together with a Cs flux of around  $10^{17} \text{ m}^{-2} \text{ s}^{-1}$  surface coatings are obtained with work function values close to those of pure bulk Cs, i. e. 2.0–2.2 eV. Under this Cs flux the low work function surface can be maintained stable for several hours of plasma exposure. Moreover, continuing plasma exposure of such a surface without further Cs evaporation can moreover preserve its work function for at least one hour. Due to comparable plasma parameters at this experiment, isotopic differences between hydrogen and deuterium discharges are limited to below the measurement accuracy of the work function diagnostic.

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- <sup>1</sup>M. Bacal and M. Wada, *Applied Physics Reviews* **2**, 021305 (2015).
- <sup>2</sup>Y. I. Belchenko, G. I. Dimov, and V. G. Dudnikov, *Nucl. Fusion* **14**, 113 (1974).
- <sup>3</sup>R. G. Wilson, *J. Appl. Phys.* **37**, 3161 (1966).
- <sup>4</sup>R. G. Wilson, *J. Appl. Phys.* **37**, 4125 (1966).
- <sup>5</sup>L. W. Swanson and R. W. Strayer, *J. Chem. Phys.* **48**, 2421 (1968).
- <sup>6</sup>H. B. Michaelson, *J. Appl. Phys.* **48**, 4729 (1977).
- <sup>7</sup>H. Yamaoka, M. Sasao, M. Wada, and H. J. Ramos, *Nucl. Instr. and Meth. in Phys. Res. B* **36**, 227 (1989).
- <sup>8</sup>Y. Mori, T. Okuyama, A. Takagi, and D. Yuan, *Nucl. Instr. and Meth. in Phys. Res. A* **301**, 1 (1991).
- <sup>9</sup>K. Shinto, Y. Okumura, T. Ando, M. Wada, H. Tsuda, T. Inoue, K. Miyamoto, and A. Nagase, *Jpn. J. Appl. Phys.* **35**, 1894 (1996).
- <sup>10</sup>T. Morishita, M. Kashiwagi, M. Hanada, Y. Okumura, K. Watanabe, A. Hatayama, and M. Ogasawara, *Jpn. J. Appl. Phys.* **40**, 4709 (2001).
- <sup>11</sup>M. Hanada, T. Seki, N. Takado, T. Inoue, T. Mizuno, A. Hatayama, M. Kashiwagi, K. Sakamoto, M. Taniguchi, and K. Watanabe, *Nucl. Fusion* **46**, S318 (2006).
- <sup>12</sup>R. H. Fowler, *Phys. Rev.* **38**, 45 (1931).
- <sup>13</sup>R. Friedl, *Rev. Sci. Instr.* **87**, 043901 (2016).
- <sup>14</sup>R. Friedl and U. Fantz, *AIP Conf. Proc.* **1515**, 255 (2013).
- <sup>15</sup>R. Friedl and U. Fantz, *Rev. Sci. Instr.* **85**, 02B109 (2014).
- <sup>16</sup>R. Gutser, C. Wimmer, and U. Fantz, *Rev. Sci. Instrum.* **82**, 023506 (2011).
- <sup>17</sup>U. Fantz, R. Friedl, and M. Fröschle, *Rev. Sci. Instrum.* **83**, 123305 (2012).
- <sup>18</sup>O. Y. Kolesnychenko, O. I. Shklyarevskii, and H. van Kempen, *Physica B: Condensed Matter* **284-288**, Part 2, 1257 (2000).
- <sup>19</sup>R. Friedl, *Experimental investigations on the caesium dynamics in H<sub>2</sub>/D<sub>2</sub> low temperature plasmas*, Ph.D. thesis, University of Augsburg (2013).
- <sup>20</sup>E. Speth, H. D. Falter, P. Franzen, U. Fantz, M. Bandyopadhyay, S. Christ, A. Encheva, M. Fröschle, D. Holtum, B. Heinemann, W. Kraus, A. Lorenz, C. Martens, P. McNeely, S. Obermayer, R. Riedl, R. Süß, A. Tanga, R. Wilhelm, and D. Wunderlich, *Nucl. Fusion* **46**, S220 (2006).
- <sup>21</sup>U. Fantz, R. Gutser, and C. Wimmer, *Rev. Sci. Instrum.* **81**, 02B102 (2010).
- <sup>22</sup>R. Friedl and U. Fantz, *AIP Conference Proceedings* **1655**, 020004 (2015).
- <sup>23</sup>D. R. Lide, ed., *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, 2005).
- <sup>24</sup>U. Fantz, S. Briefi, D. Rauner, and D. Wunderlich, *Plasma Sources Science and Technology* **25**, 045006 (2016).
- <sup>25</sup>K. Jousten, ed., *Wutz Handbuch Vakuumtechnik*, 10th ed., Vieweg+Teubner Praxis (Vieweg+Teubner, Wiesbaden, 2010).
- <sup>26</sup>P. W. v. Amersfoort, Y. C. Tong, and E. H. A. Granneman, *J. Appl. Phys.* **58**, 2317 (1985).
- <sup>27</sup>S. Cristofaro, R. Friedl, and U. Fantz, accepted for publication in *AIP Conference Proceedings* (2017).