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Ultra-low work function of caesiated surfaces and impact of selected gas species

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Abstract: Modern high-power negative hydrogen ion sources rely predominantly on the surface production of negative hydrogen ions. Hence, low work function converter surfaces are mandatory, for which the alkali metal Cs is commonly evaporated into the ion source to lower the work function of refractory metals by surface adsorption. To study the work function behaviour upon caesiation under the typically given non-ultra-high vacuum conditions, investigations are performed at a dedicated laboratory experiment. In a vacuum environment dominated by water vapour, the work function evolution is found to be dependent on the flux ratio of Cs to H_2O onto the surface. For sufficiently high flux ratios, ultra-low work functions in the range of 1.25 ± 0.10 eV are generated with excellent reproducibility. In the absence of Cs evaporation, the work function gradually increases under the influence of the residual gases, and re-caesiation processes lead to lower quantum efficiencies and higher work functions of typically 1.9–2.1 eV. While the addition of hydrogen and deuterium gas at several Pa as well as the leakage of inert gases (argon and nitrogen) into the vacuum system have a negligible influence on the caesiation process, small amounts of oxygen with partial pressures of $\sim 10^{-2}$–10^{-1} Pa lead to an instant reduction of the Cs density in the gas phase by several orders of magnitude and to an increase in the work function of the order of 1 eV. After the oxygen exposure is terminated, however, the Cs density and work function fully recover within several minutes.

Keywords: Ion sources (positive ions, negative ions, electron cyclotron resonance (ECR), electron beam (EBIS)); Photoemission

Contents

1 Introduction

Negative hydrogen ion sources based on the surface production mechanism require extraction electrode surfaces with a low work function. To achieve this, Cs with a bulk work function of 2.0–2.1 eV [1, 2] is commonly evaporated into the source. The Cs deposition on the extraction electrode surface (typically Mo) leads to a significant increase in the extracted negative ion current as well as to a decrease in the co-extracted electron current [3, 4]. The Cs surface chemistry in an ion source environment is, however, complex due to the influence of various particle species. During vacuum phases, typically non-ultra-high vacuum conditions are given, i.e., the amount of residual gases is not negligible and the formation of Cs compounds is likely due to the high chemical reactivity of Cs. During plasma phases, the Cs coating is exposed to fluxes of hydrogen molecules, atoms, ions and photons, and an effective redistribution of (ionised) Cs (compounds) within the source is driven. Hence, the Cs layer and its work function are subject to temporal changes [5]. Information on the work function of the caesiated converter surface in ion sources is unfortunately sparse because the development of a reliable work function diagnostic is challenging in the harsh ion source environment [6]. Therefore, work function investigations are performed at the flexible laboratory experiment ACCesS, which is equipped with a finely adjustable Cs oven and a comprehensive set of diagnostic systems [5]. The present paper is dedicated to investigations on the work function behaviour of metal surfaces upon caesiation and re-caesiation processes under vacuum conditions of 10^{-6}–10^{-5} mbar, which is of particular interest for negative ion sources for neutral beam injection systems for nuclear fusion experiments [4]. Furthermore, the influence of selected impurity gases on the caesiation process is studied.

2 Experimental setup

The ACCesS experiment is schematically illustrated in figure 1. It consists of a cylindrical stainless steel vacuum vessel with an inner diameter of 15 cm and a height of 10 cm, which is evacuated by a turbomolecular and roughing pump to a background pressure of 10^{-6}–10^{-5} mbar (limited by Viton O-ring seals). The background pressure is monitored with a cold cathode gauge and the composition of the residual gas can be measured with a differentially pumped residual gas analyser (RGA, not calibrated for absolute partial pressures). As the residual gas is clearly dominated by water vapour, the background pressure can be approximated by the partial pressure of H_2O. Cs is evaporated into the experiment by means of a Cs oven [7] attached to the bottom plate of the vacuum vessel. The nozzle of the oven is directed towards a sample holder, which is mounted with a ceramic block on the bottom plate to ensure electrical and thermal insulation. The support area of the sample holder is $44 \times 30\,\text{mm}^2$ and can be heated up to $1000\,°\text{C}$. Samples are attached with clamps to the sample holder and the temperature of the sample's surface is measured with a K-type thermocouple. The density and temperature of neutral Cs atoms in the gas phase are measured by means of a tunable diode laser absorption spectroscopy (TDLAS) system [8] along a diagonal line of sight (LOS) through the vacuum vessel, which is in parallel to and at a distance of about 2 cm from the sample holder. The detection limit for the LOS-averaged Cs density is about $2 \times 10^{13}\,\text{m}^{-3}$ and the Cs flux onto the sample holder is calculated under the assumption of an isotropic thermal distribution of velocities. Gas feeding is done via calibrated mass flow
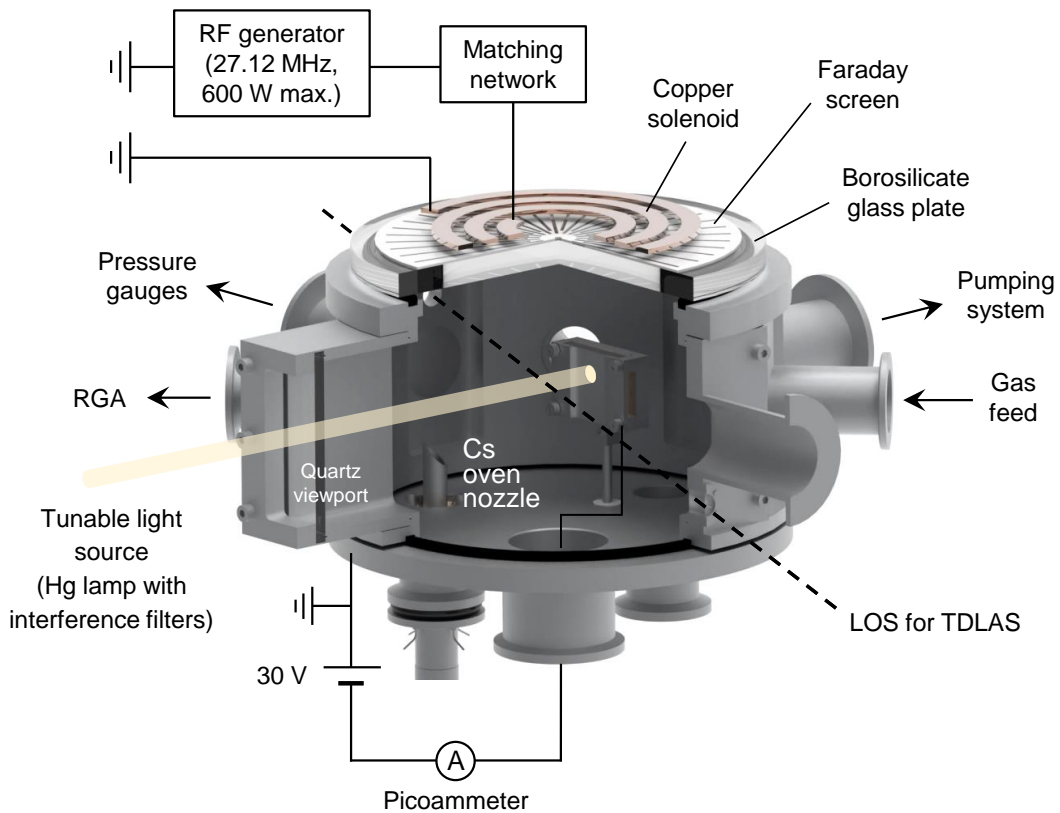

Figure 1. Illustration of the experimental setup including the arrangement of the applied diagnostic systems.

controllers and the absolute pressure in the vacuum system during gas flow is measured with a capacitance manometer. Plasmas can be generated via inductive radio frequency (RF) coupling by using a planar copper solenoid on top of the vessel and an RF generator operating at 27.12 MHz (600 W maximum output power). As dielectric between the antenna and the vacuum, a Borosilicate glass plate is used.

The work function of installed sample surfaces at the sample holder is measured in situ by using the photoelectric effect. For this, a high pressure mercury lamp in combination with 20 interference filters (10 nm FWHM) is used as tunable light source, providing mean photon energies in the range of 5.04–1.45 eV with an energy resolution of mostly 0.1–0.3 eV. The radiation is collimated via quartz lenses and guided through a quartz viewport onto the sample surface (spot diameter ≈ 15 mm, radiant powers ∼ 0.1–1 mW), and the photoelectrically emitted electrons are drawn to the grounded vessel walls by applying a bias of −30 V to the sample holder and surface. The photocurrents are measured with a Keithley 6487 picoammeter (dark current typically in the range of 10^{-11}–10^{-10} A) and the evaluation of the photocurrents is done according to the Fowler theory [9], yielding work functions with an uncertainty of about ±0.1 eV. The diagnostic was lately improved with respect to the threshold sensitivity, which is described in detail in [10].

3 Formation of ultra-low work function layers

In figure 2, a compilation of work function data from several caesiations performed on polycrystalline Mo and stainless steel surfaces at room temperature is presented. To ensure reproducibility, the different caesiations (indicated by the different symbols) are started each time from a Cs-free source and after the application of a hydrogen plasma (10 Pa gas pressure, 250 W RF power) for a couple of hours one day before the caesiation, which is done to remove adsorbed impurities from ambient air from the substrate surface. In the left diagram, the work function is plotted as a function of the applied neutral Cs density in the gas phase. Under consideration that the correlation between the measured work function and Cs density underlies a larger uncertainty during the initial ramp-up phase of the caesiation process [10], an excellent reproducibility is given: the work function is reduced to about 2 eV with Cs densities of a few 10^{14} m^{-3} and to ultra-low values of 1.25 ± 0.10 eV with Cs densities $\gtrsim 10^{15}$ m^{-3}, independent of the substrate material. Further campaigns have shown that these ultra-low values cannot be reached by increasing the Cs fluence with a lower Cs density instead. As explained in detail in [10], the generation of ultra-low work functions is attributed to the formation of Cs oxides upon reaction of Cs with residual H_2O. Consequently, the proposed figure of merit for the achievable work function is the flux ratio of Cs to H_2O onto the surface. By plotting the compiled work function data against this flux ratio as shown in the right diagram of figure 2, a threshold flux ratio of $\Gamma_{Cs}/\Gamma_{H_2O} \sim 5 \times 10^{-3}$ is determined to reach a work function of 1.25 eV. For $\Gamma_{Cs}/\Gamma_{H_2O} > 5 \times 10^{-3}$, the evaluated work function remains constant within the error bars. However, it should be mentioned that the photocurrents for photon energies close to the work function increase, i.e., 1.25 eV might be an upper limit here. In this case, interference filters with transmissions below 1.45 eV would be needed for a more accurate determination of the work function, for which, however, another light source with stronger emission in the infrared range would be required as well.
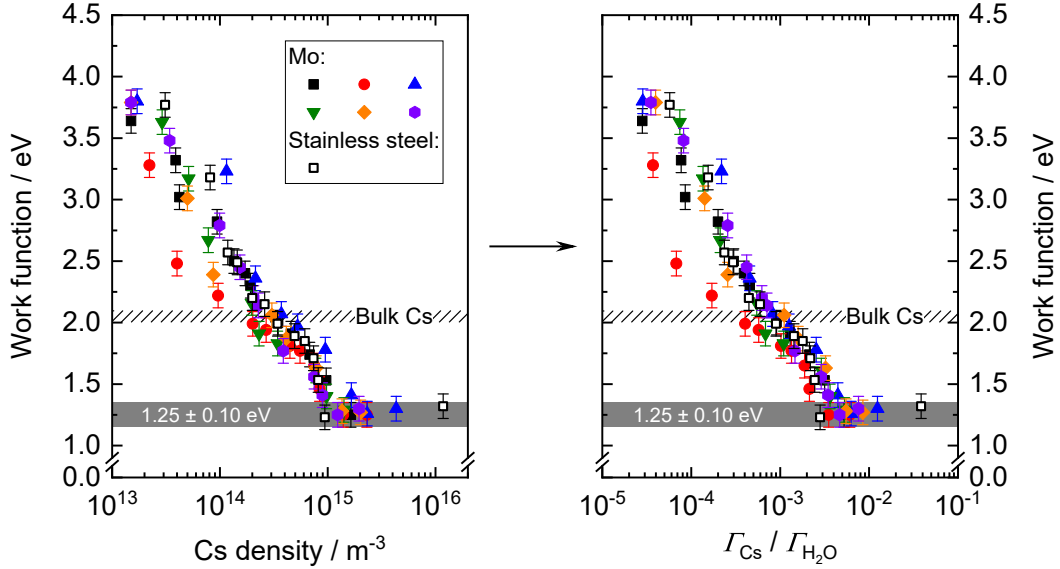
Figure 2. Compilation of work function data measured during the first caesiation of Mo and stainless steel surfaces. The different symbols represent different caesiations, each time starting from a Cs-free source and with a background pressure in the range of 10^{-6}–10^{-5} mbar. The work function is plotted as a function of the neutral Cs density in the left diagram and as a function of the flux ratio of neutral Cs atoms to residual water molecules in the right diagram.

4 Degradation and re-caesiation

The work function in the range of 1.25 ± 0.10 eV is kept stable as long as the Cs density is sustained at $\gtrsim 10^{15}$ m^{-3} in the gas phase (tested up to a few hours). When the Cs density is reduced below $\sim 10^{15}$ m^{-3}, the work function starts to increase, and after the Cs evaporation is stopped, the work function increases to 2.6–2.7 eV on the hour scale. Afterwards, the degradation slows down, and work functions of 2.8 and 3.5 eV are obtained after one day and a few weeks, respectively. The gradual increase in the work function is explained by the continuous accumulation of residual gases, changing the chemical composition and stoichiometry at the surface.

Upon re-caesiation at identical vacuum conditions, the work function behaviour is significantly different from the first caesiation. This is demonstrated in figure 3(a), where the evolution of the work function of a stainless steel surface upon its first caesiation is compared to the one upon re-caesiation after 19 days of degradation, with the background pressure being stable at 6–7×10^{-6} mbar throughout the whole time. The work functions and Cs densities are plotted against the Cs fluence Φ_{Cs}, which is defined as the time integrated Cs flux and is thus a measure of the total amount of Cs atoms to which the surface is exposed during the caesiation process. As can be seen, the Cs density vs fluence traces of the two caesiation processes are almost identical, i.e., similar Cs densities are applied for comparable time periods. While the work function before the first caesiation is about 4.0 eV, it is 0.5 eV lower before the re-caesiation. Upon the first caesiation, the work function follows the behaviour as shown in figure 2: a value of about 2.2 eV is reached with a Cs density of 3×10^{14} m^{-3} ($\Phi_{Cs} = 2 \times 10^{19}$ m^{-2}), and the subsequent increase in the Cs density to 10^{15} m^{-3} and beyond leads to work functions in the range of 1.25 ± 0.10 eV ($\Phi_{Cs} \gtrsim 2 \times 10^{20}$ m^{-2}). Upon re-caesiation, a work function of 2.2 eV is reached after the application of a comparable Cs fluence. Afterwards, however, the work function remains constant at
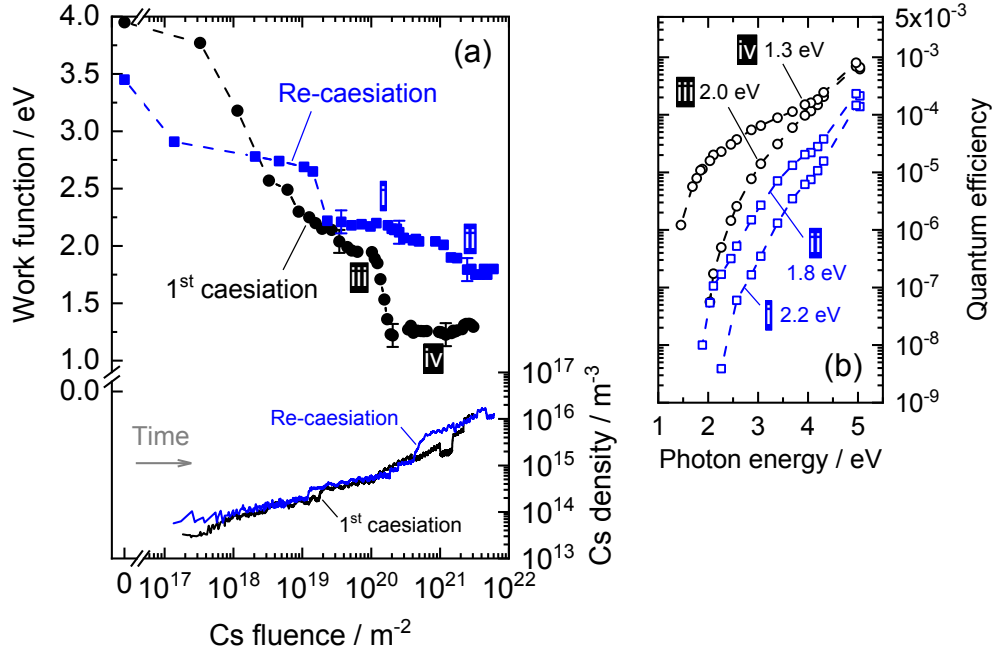
Figure 3. (a) Work function evolution during the first caesiation of a stainless steel substrate and during its re-caesiation after 19 days in vacuum. The work functions as well as the neutral Cs densities applied during the caesiation processes are plotted against the calculated Cs fluence. In (b), QE curves recorded at different times during the first caesiation and re-caesiation are shown, and the corresponding work functions are indicated.

$2.2 \pm 0.1\,\text{eV}$ up to $\Phi_{\text{Cs}} \approx 2 \times 10^{20}\,\text{m}^{-2}$, and by keeping the Cs density at $\sim 10^{15}\,\text{m}^{-3}$ for some minutes, the work function gradually decreases to 2.0–2.1 eV. By increasing the Cs density up to $\sim 10^{16}\,\text{m}^{-3}$, the work function is reduced further to a minimum value of about 1.8 eV ($\Phi_{\text{Cs}} > 2 \times 10^{21}\,\text{m}^{-2}$).

In figure 3(b), photoelectric quantum efficiencies (QEs) measured during the first caesiation and re-caesiation are plotted as a function of the photon energy ε_{ph}. The QEs are calculated by

$$\text{QE}(\varepsilon_{\text{ph}}) = \frac{\varepsilon_{\text{ph}} I(\varepsilon_{\text{ph}})}{e P(\varepsilon_{\text{ph}})}, \tag{4.1}$$

where P denotes the radiant power of the irradiating light, I the photocurrent, and e the electron charge. As can be seen, the work function decrease from 2.2 to 1.8 eV during the re-caesiation process is accompanied by an increase in the QE throughout the accessible spectral range (curves labeled i and ii). Also plotted are the QE curves recorded during the first caesiation at a work function of 2.0 eV (labeled iii) and 1.3 eV (labeled iv, photoelectric response obtained with all 20 interference filters). The comparison shows that at a reached work function of 1.8 eV during the re-caesiation, the QEs for $\varepsilon_{\text{ph}} \geq 2.0\,\text{eV}$ are still lower compared to the surface with a work function of 2.0 eV obtained during the first caesiation. Furthermore, the QE at $\varepsilon_{\text{ph}} = 1.9\,\text{eV}$ (close to the evaluated work function) is three orders of magnitude lower compared to the surface with a work function of 1.3 eV, which is obtained during the first caesiation with even lower Cs fluxes and fluences.

The measurements impressively demonstrate that in the absence of Cs evaporation, the residual gases (mainly H_2O) alter the properties of the caesiated surface in a way that reduces the QE and prevents the re-establishment of an ultra-low work function coating upon re-caesiation. Various conducted re-caesiations of Mo substrates after different degradation times (few days up to several

weeks) confirmed this behaviour, with the actual QE and work function evolution being dependent on the experimental history of the substrate (e.g., degradation time and plasma exposure). It is speculated that the adsorption of Cs atoms on degraded caesiated surfaces produces much weaker electrostatic dipoles compared to the adsorption on uncaesiated metal substrates, leading to a different surface chemistry and thus to an influence on the structural and chemical composition of the growing Cs layers. Typically, work functions in the range of 1.9–2.1 eV are measured with applied Cs densities of the order of $10^{15}\,\text{m}^{-3}$ upon re-caesiation.

5 Influence of gas exposure

Apart from residual gases, the surface upon caesiation is exposed to hydrogen gas at negative hydrogen ion sources. Furthermore, impurity gases might leak into the system. Therefore, a clear understanding of the impact of various gas species on the work function of caesiated surfaces is indispensable and studied in the following.

5.1 Hydrogen

No influence on the condition of the caesiated surface is detected when pure H_2 gas is introduced into the vacuum chamber during a caesiation process (tested with gas pressures up to 10 Pa). The measured photocurrents before and after the gas feeding are comparable and the respective Fowler evaluations yield the same work functions within the uncertainty of ± 0.1 eV. As negative ion sources for fusion must in particular operate in deuterium [4], investigations with D_2 gas feeding were performed as well, and the same result as with H_2 is obtained.

5.2 Inert gases

The influence of noble gases on the caesiation process is of particular interest for negative ion sources for fusion since He from the fusion reactor might enter the beamline. Furthermore, the application of non-evaporable getter (NEG) pumps is considered [11], which are not able to pump noble gases. To gain insight into the impact of small amounts of noble gases on the caesiation process, investigations with an elevated partial pressure of Ar were conducted at ACCesS. During a caesiation process, the regular pumping system was separated from the vacuum chamber by closing a gate valve and the pumping was only done by an attached NEG pump (CapaciTorr® HV 200) from the company SAES Getters. During the time when only the NEG pump is attached to the chamber, the RGA recording reveals that Ar gas (contained in ambient air at 0.9 %) permeates through the Viton seals. Additionally, an increase in the RGA signal for He (0.0005 % in air) is observed, but is much less pronounced. After a few minutes, the gradually increasing Ar content in the chamber determines the background pressure, and after two hours, the partial pressure of Ar is about 3×10^{-2} Pa. Nonetheless, the Cs density in the gas phase stays constant (with the operating parameters of the Cs oven remaining unchanged) and the photoelectric threshold of the caesiated surface is not affected. Hence, no indications are given that impairing chemical reactions between Cs and Ar occur.

As an elevated partial pressure of Ar is not harmful to the caesiation process, it is expected that also an increased partial pressure of He is unproblematic. In addition, investigations with the introduction of small amounts of N_2 have shown that virtually no influence on the Cs density in the gas phase or on the work function of caesiated surfaces is given. However, it must be considered that ionised gases

with masses higher than hydrogen (deuterium) can strike the caesiated surface in the plasma phase with several eV so that higher Cs removal rates might be given due to an enhanced sputtering yield.

5.3 Oxygen

In contrast to hydrogen and inert gases, the Cs density in the gas phase and the work function of caesiated surfaces are heavily affected when O_2 leaks into the vacuum system. This is demonstrated in figure 4(a), where O_2 is introduced during the caesiation of a Mo substrate. The partial pressure of O_2 increases to $\sim 10^{-1}$ Pa in the moment the mass flow controller opens (initial overshoot) and decreases to slightly above 10^{-2} Pa shortly afterwards. In the moment O_2 enters the vacuum chamber, the Cs density of about 1.5×10^{15} m^{-3} instantly drops below the TDLAS detection limit of 2×10^{13} m^{-3}, and the measured work function about half a minute later lies 1 eV above the initial value of 1.4 eV. During the next 17 min, the partial pressure of O_2 is kept constant and the work function continues to increase, with a gradually decreasing slope. The slope increases again by increasing the O_2 partial pressure, which is demonstrated at $t \approx 32$ min where the partial pressure is elevated to 3.5×10^{-2} Pa. After the O_2 inlet is terminated, the work function is 3.5 eV. The total O_2 fluence to which the caesiated surface is exposed is about 5×10^{23} m^{-2}, which is comparable to the fluence of residual H_2O after about 8 h at a base pressure of 5×10^{-6} mbar, after which the work function is typically not higher than 3 eV. Hence, the degradation of caesiated surfaces upon O_2 exposure is more pronounced than upon H_2O exposure.

Since the Cs density is diminished by at least two orders of magnitude in less than one second when O_2 enters the vacuum chamber, considerable chemical reaction kinetics are present. After the O_2 exposure is stopped, it takes about 6 min for the TDLAS signal to reappear and about 18 min until the Cs density is about the same as before the O_2 inlet. The time it takes for the Cs density to reestablish depends on the amount of O_2 that is introduced into the vacuum chamber. In figure 4(b), measurements are shown where the O_2 gas feed is opened several times for only a few seconds
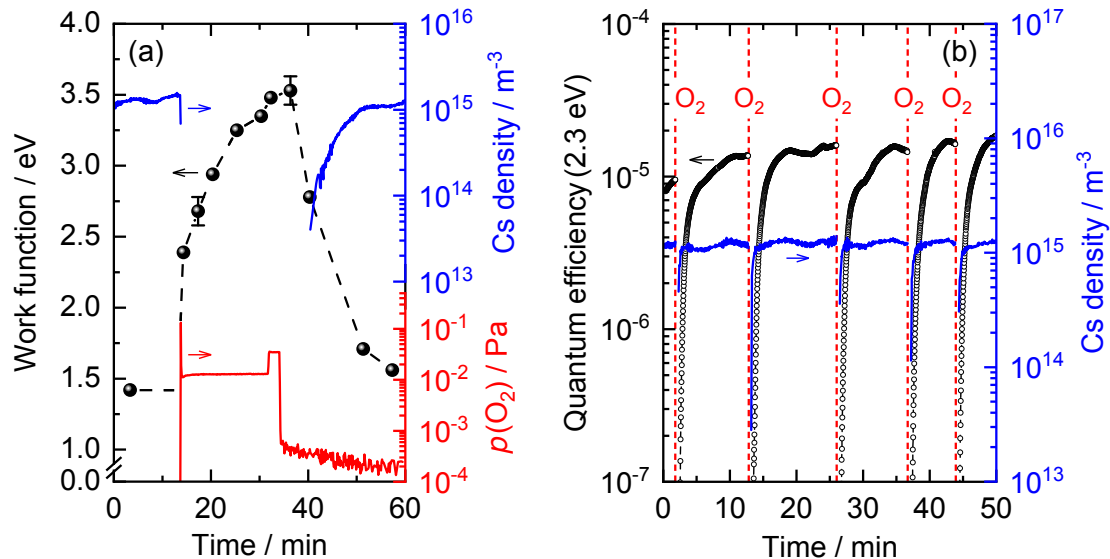

Figure 4. (a) Behaviour of the work function of a caesiated Mo surface and neutral Cs density in the gas phase during and after an elevated partial pressure of O_2 in the vacuum chamber. (b) Evolution of the QE for 2.3 eV photons of a caesiated Mo surface and neutral Cs density upon repetitive O_2 exposures.

(pressure increase to $\sim 10^{-1}$ Pa comparable to the overshoot in figure 4(a), estimated fluence per dose $\sim 10^{22}\,\mathrm{m}^{-2}$), and the times for the TDLAS signal to reappear and the Cs density to fully recover are typically about 30 s and 1–2 min, respectively.

Before the TDLAS signal reappears in figure 4(a), the work function is 3.5 eV and a substantial amount of oxygen is expected to be adsorbed at the sample surface. By the re-establishment of the Cs flux onto the surface, the work function decreases remarkably fast and a value of 1.6 eV is measured after 17 min. When the caesiated surface degrades to a work function of 3.5 eV within several days due to the exposure to residual gases from the background pressure and is subsequently re-caesiated, such a rapid decrease in the work function is not observed (cf. figure 3). The fast recovery of the caesiated surface after O_2 exposure becomes also evident from figure 4(b): here, the QE at 2.3 eV is continuously monitored with a time resolution of 1 s. An instant drop below the detection limit is given every time O_2 gas is added, and by the subsequent re-establishment of the Cs flux onto the surface, the QE is (more than) fully recovered within a couple of minutes. Therefore, it is suggested that the adsorption of O_2 on the caesiated surface facilitates the formation of strong dipoles and Cs oxides (e.g., Cs_2O) upon re-caesiation [12].

6   Conclusions and outlook

The discovery of how to reliably generate Cs layers with work functions far below the one of bulk Cs under moderate vacuum conditions advances the understanding of the properties of caesiated surfaces for ion source applications, in particular for ion sources for fusion. The proposed figure of merit for the achievable work function is the flux ratio of Cs to residual H_2O onto the surface, which must be $\gtrsim 5 \times 10^{-3}$ to reach minimum values in the range of 1.25 ± 0.10 eV. At the ion sources of the BATMAN Upgrade (BUG) and ELISE test facilities where operational scenarios for the ITER neutral beam injection systems are developed [4], this flux ratio is typically in the range of 3–9×10^{-3} during vacuum phases (Cs density $\sim 5 \times 10^{13}\,\mathrm{m}^{-3}$, base pressure 1–5×10^{-7} mbar), which implies that the growth of ultra-low work function coatings can be expected on the extraction electrode surface. By the application of a newly developed photoelectric work function measurement system based on LEDs, such low work functions have recently been confirmed in the BUG ion source [13].

In the absence of Cs evaporation, the residual gases cause a gradual increase in the work function that cannot be fully reversed via re-caesiation. Additional amounts of O_2 with partial pressures of $\gtrsim 10^{-2}$ Pa also adversely affect the caesiated surfaces, as the work function increases on the order of 1 eV. The initial equilibrium can, however, be regained after the elevated O_2 content is pumped out, with the recovery time being dependent on the totally entered amount of O_2 into the source. Nevertheless, an undesirable increase in the Cs consumption and a prolonged conditioning time of the surface would be the result. In contrast, an elevated partial pressure of Ar and N_2 as well as the addition of H_2 and D_2 gas of several Pa is not harmful to the caesiation process.

Future studies will focus on the influence of selected plasma species as well as plasma exposure on the work function dynamics of caesiated surfaces. Furthermore, investigations on the Cs layer growth in a vacuum environment ranging from 10^{-6} mbar to the ultra-high vacuum regime ($\lesssim 10^{-9}$ mbar) are foreseen, as the background pressure in present-day ion sources ranges from about 10^{-10} to 10^{-6} mbar depending on the application.

Acknowledgments

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