Pumping and electron-stimulated desorption properties of a dual-layer nonevaporable getter

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The ASTeC Vacuum Science Group has an ongoing study for the improvement of the nonevaporable getter (NEG) coatings currently used in many accelerators around the world. The main advantages of using NEG coatings are evenly distributed pumping speed, low thermal outgassing rates, and low photon-stimulated gas desorption and electron-stimulated gas desorption (ESD). Previously, it was shown that the dense NEG coating provides lower ESD compared to that of a columnar film, but its pumping properties are reduced. This paper describes the results for a dual layer of NEG where a dense layer was deposited first and a columnar layer was then deposited on top. In such a dual-layer NEG coating, the dense layer acted as a barrier for hydrogen diffusion and the columnar layer further reduced the ESD of hydrogen and provided improved pumping properties. An alloy target of Ti-Zr-Hf-V was used to deposit a $0.5\,\mu$m-thick layer of the dense NEG followed by a $1\,\mu$m-thick columnar structure of NEG onto the inner surface of a 50-cm long stainless steel tube. The composition and the structure of the dual layer were determined by energy dispersive x-ray spectroscopy and scanning electron microscopy, respectively. The NEG vacuum performance was tested using the ESD and pumping properties, which were measured on a dedicated in-house designed facility. © *2016 American Vacuum Society.*
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I. INTRODUCTION

Since their invention in 1990s,[1–3] nonevaporable getter (NEG) coatings have become an important vacuum technology used in particle accelerators.[4–7] The ultrahigh vacuum (UHV) and extreme high vacuum conditions along the beam vacuum chamber are specified by a tolerable beam–gas interaction rate. These conditions can be met due to the main NEG coating properties: distributed pumping speed[1–3,8] as well as low thermal outgassing rates[2,3] and particle-induced[9–11] desorption yield compared to uncoated typical technical metals used for vacuum chamber. In many cases, these properties provide the only solution in a conductance-limited environment.[4] It is also the most cost effective method for achieving the specified gas density.[7,12]

The gas density of H_2, CO, and CO_2 along an accelerator vacuum chamber coated with NEG is proportional to the ratio of the desorption yield η and the sticking probability α for these gases: $n \propto \eta/\alpha$.[13,14] Previous studies have determined that the columnar structure of the NEG film provides a greater sticking probability and capacity than a dense NEG film.[8,15,16] The highest pumping properties were obtained with a quaternary Ti-Zr-Hf-V film with a columnar structure deposited from an alloy target.[17] However, the lowest electron-stimulated gas desorption (ESD) yields were achieved with a quaternary Ti-Zr-Hf-V film with a dense structure deposited from an alloy target.[18,19] This is due to the nature of the dense film as a superior barrier for hydrogen diffusion from the vacuum chamber material into the vacuum. By combining the low ESD yield of the dense film and the highest pumping properties of the columnar film, one may be able to achieve an even lower gas density.

II. EXPERIMENT

A. Sample deposition and surface analysis

A dual layer of NEG was deposited on an internal surface of a 0.5-m long and 38-mm diameter 316LN stainless steel tube. A 3-mm diameter alloy target of Ti-Zr-Hf-V comprising equal proportions of 25 at. % for each element was used to deposit $0.5\,\mu$m of dense NEG, followed by $1\,\mu$m of columnar structure, as determined with a scanning electron microscope (SEM) and shown in Fig. 1. The depositions were performed in the solenoidal magnetron deposition facility, as described in detail in Ref. 16. The depositions were carried out under the same conditions as used in our previous experiments:[18] a partial pressure of 10^{-2} mbar of research-grade Kr gas, a deposition temperature of $110\,^{\circ}$C, and using a DC and a pulsed DC mode to produce the columnar and the dense thin film structures, respectively. The tube was baked prior to deposition, and the base pressure was 10^{-10} mbar. Two test pieces of Si and stainless steel were deposited upon simultaneously, and were used to determine the film morphology and structure. The composition and the structure of the dual layer were determined by energy dispersive x-ray spectroscopy, which confirmed that the deposited film possessed the same stoichiometric composition as the target.

B. NEG evaluation setup and formulae

The NEG ESD and pumping properties were measured on a dedicated in-house designed facility shown in Fig. 2. The details of the facility design and a model employed for the ESD yields calculations are described in detail in Ref. 20,

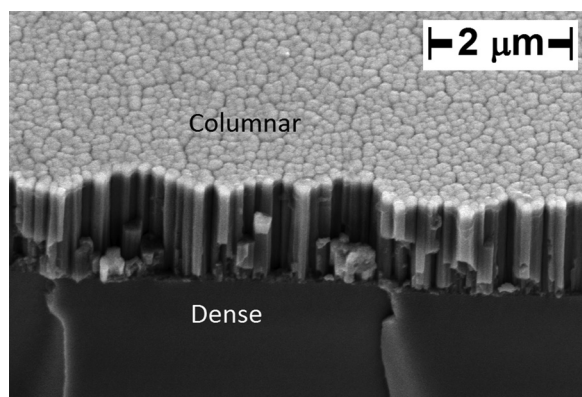[a]Electronic mail: oleg.malyshev@stfc.ac.uk

FIG. 1. Cross-section SEM micrograph of a dual-layer film.

and a method and the modeling results for the sticking probability calculations are described in Ref. 21. Pressures P_1 and P_2 are measured with residual gas analyzers (RGA) in the test chamber and used for the ESD yields and sticking probability calculations. The gas injection line is used for a selected gas injection for the sticking probability and pumping capacity measurements. Sticking probability is estimated from the pressure ratio and P_2/P_1 using the results from test particle Monte-Carlo modeling.[21] The amount of injected gas and injected gas flow are calculated from the measured pressure and known volume in the injection line. The pumping line is used for pumping the test chamber during initial pumping down and bakeout/activation procedure (the roughing pumping line) and during ESD measurements (the UHV pumping line).

The ESD yields are calculated with two formulas. The ESD yields for gases which are not pumped by NEG coating (such as CH_4 and noble gases) are calculated with

$$\eta_M = [\Delta P_{1,M} - \Delta P_{2,M}] \frac{2 U_M q_e}{k_B T I}, \tag{1}$$

and the ESD yields for gases which are pumped by NEG coating (such as H_2, CO, CO_2, and H_2O) are calculated with

$$\eta_M = \left[\Delta P_{1,M} + \frac{\Delta P_{1,M} - \Delta P_{2,M}}{\cosh\sqrt{\frac{\alpha_M C_M}{U_M}} - 1} \right] \frac{\alpha_M C_M q_e}{k_B T I}, \tag{2}$$

where ΔP [mbar] is the pressure difference measured during and before electron bombardment, U [m³/s] is the sample tube conductance, α_M is the sample tube wall (NEG coating) sticking probability, $C_M[m^3/s] = \pi d L v_M/4$ is ideal sample wall pumping speed, where d and L are an inner diameter and an axial length of the sample tube and v_M is a mean velocity of gas M molecules.

C. Experimental procedure for vacuum properties evaluation

The produced tubular sample with 1.5 μm thick dual NEG layer was moved to the NEG ESD and pumping properties facility for vacuum properties evaluation. The same sample was used for all measurements described in this paper. The experimental procedure includes the following steps:

(1) Sample installation (run 1) or air vent (runs 6 and 11) followed by pumping down below 10^{-6} mbar.
(2) Vacuum system bakeout and/or NEG coating activation:
  – For runs 1, 6, and 11 only: Vacuum system bakeout to 250 °C for 24 h (with a ramp-up and -down rate of 50 °C/h) after installing the sample or venting it to air. During this bakeout, the NEG-coated sample was ramped up together with the vacuum system and kept at 80 °C for 31 h.
  – In run 10 this step was omitted.
  – For other runs: The NEG activation to a selected temperature (150, 180, 250, and 350 °C for 24 h with a ramp-up and -down rate of 50 °C/h).
(3) The ESD measurement using electrons at energy of 500 eV.
(4) The H_2 initial sticking probability measurement and the CO initial sticking probability and pumping capacity measurement followed by a full saturation of the NEG coating with CO.
(5) After runs 5 and 10, starting from item (1). For other runs, starting from item (2).

The vacuum system was vented to air for 5 min between runs 5 and 6 and runs 10 and 11 to determine whether this was sufficient to bring the sample to its initial condition. This procedure was repeated twice (see Table I).
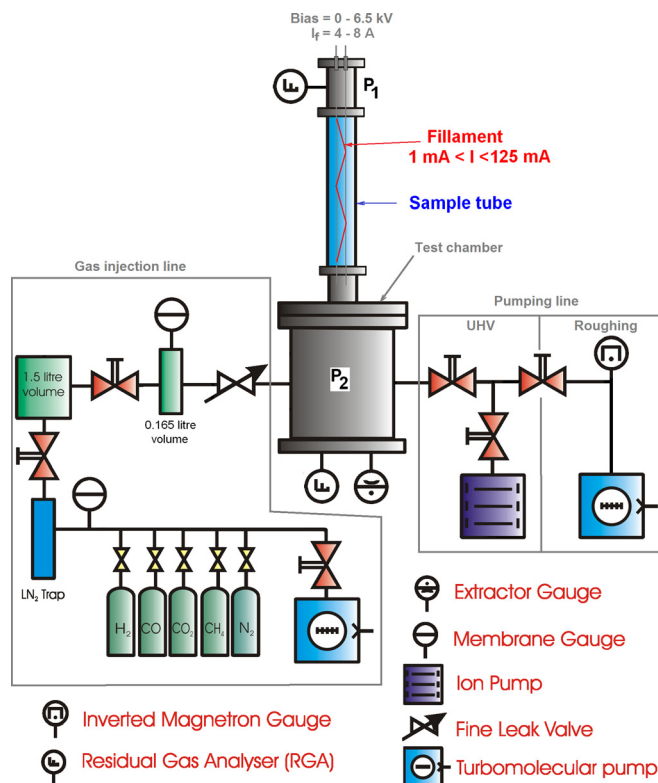

FIG. 2. (Color online) Layout of the facility for NEG ESD and pumping property measurements on tubular samples. Turbomolecular pumps are backed with scroll pumps (not shown).

TABLE I. Sticking probabilities for different gases and the CO sorption capacities for the samples activated at different temperatures, T_a.

			Sticking probability			
Run no	Initial condition	T_a (°C)	H_2	CO	CO_2	CO sticking capacity (ml)
1	As-received	80	1.5×10^{-3}	1.1×10^{-2}	4.5×10^{-2}	—
2	CO saturated	150	9×10^{-3}	5.5×10^{-2}	0.1	0.3
3	CO saturated	180	1.8×10^{-2}	7.5×10^{-2}	0.11	0.5
4	CO saturated	250	2.3×10^{-2}	8.5×10^{-2}	0.2	3
5	CO saturated	350	3.0×10^{-2}	0.11	0.2	10
6	Vented to air	80	1.5×10^{-3}	5×10^{-3}	4.5×10^{-2}	—
7	CO saturated	150	1.0×10^{-2}	5.5×10^{-2}	0.1	0.2
8	CO saturated	180	1.8×10^{-2}	7.5×10^{-2}	0.11	0.8
9	CO saturated	250	2.0×10^{-2}	0.18	0.2	2.5
10	CO saturated	20	1.2×10^{-2}	0.11	0.11	0.3
11	Vented to air	80	1.4×10^{-3}	4×10^{-3}	4.5×10^{-2}	—
12	CO saturated	150	1.5×10^{-3}	5.5×10^{-2}	0.1	0.2
13	CO saturated 1 year pumping	180	5×10^{-3}	8.5×10^{-2}	0.11	0.8
14	CO saturated	250	8×10^{-3}	0.14	0.15	2

Run 10 aims to observe the behavior of a CO-saturated NEG coating without activation. The vacuum system was exposed to CO at a pressure $P = 10^{-3}$ mbar for 10 min and then was pumped down with a turbomolecular pump for 2 h reaching pressure of 4×10^{-10} mbar prior to the beginning of the ESD measurements.

After run 12, the vacuum system with a sample held pumped with a sputter ion pump for a year at a pressure $\sim 10^{-10}$ mbar, after which it was activated at 180 °C for 24 h.

The ESD yields were measured as a function of electron dose. The results for runs 1–6 are shown in Fig. 3. These results can be compared with our earlier results for single-layer dense and columnar films.[19] A comparison of the ESD yields as a function of electron dose for samples activated at 80, 150, and 180 °C is shown in Fig. 4, and the sticking probabilities for H_2 and CO and the sorption capacity for CO are shown in Table I.

III. DISCUSSION

The ESD yields of a dual-layer film in runs 2–4 shown in Fig. 3 can be compared to the single-layer results given in Fig. 3 of Ref. 18 measured at exactly the same conditions. The ESD yields for H_2 and CO at electron dose of 10^{21}, 10^{22}, 10^{23}, and 10^{24} e$^-$/m^2 are summarized in Table II. It can be seen that the ESD yields of the dual layer are either better or comparable to those of a single layer. The pumping properties for a dual-layer film are better than those for a single-layer dense film, but are lower than or comparable to a single-layer columnar film (cf. Table I in the present work and Table 1 in Ref. 18). The latter result can be explained by the variations in pumping properties present between samples. In general, the combined vacuum performance (η/α) of a dual-layer film is better than both single-layer films, i.e., the same activation procedures for a dual-layer film will provide lower pressures under electron bombardment than

a single-layer film in a wide range of electron doses from the initial dose (just after activation) to 10^{24}–10^{25} e$^-$/m^2. Because the photon-stimulated desorption process occurs mainly in the two steps of photoelectron production and electron-stimulated desorption, a dual-layer film will be beneficial under synchrotron radiation as well.

It is also interesting to compare the results from a dual-layer film with those from single-layer films deposited on vacuum-fired stainless steel vacuum chambers.[19] It can be seen that a single-layer dense film on vacuum-fired stainless steel provides comparable or lower ESD yields, though its pumping properties are not as good as those of the dual-layer film. By comparing three sets of results, comprising those reported in this paper and the two sets of data in Refs. 18 and 19, it can be concluded that if the NEG coating provides an insufficiently low pressure, then further ESD reduction could be achieved by certain procedures. These procedures are herein set out in the order of their efficiency: (1) using a dense NEG coating instead of a columnar one,[18] (2) using a dual-layer NEG coating (demonstrated in this paper), (3) vacuum firing the vacuum chamber before NEG deposition,[19] and (4) using a dual-layer NEG coating deposited on a vacuum-fired vacuum chamber [the latter is a logical conclusion of the previous (1)–(3) item and should be examined in the future studies].

The optimum activation temperature for the dual-layer NEG coating depends on application and should be chosen by a user based on the following considerations. The NEG activation at 150 °C in run 2 rendered the lowest value of $\eta(H_2)$ after a dose of 10^{24} e$^-$/m^2 when compared to runs 1 at a lower activation temperature and runs 3–5 at a higher activation temperature, though this was not true for other gas species. The NEG activation at 180 °C in run 3 provided the lowest initial $\eta(H_2)$ and $\eta(CO)$ values; but $\eta(H_2)$ reached its lowest value at a dose of $D = 4 \times 10^{22}$ e$^-$/m^2, and then increased until $D = 6 \times 10^{23}$ e$^-$/m^2 and decreased again at higher doses. This kind of behavior of $\eta(H_2)$ for
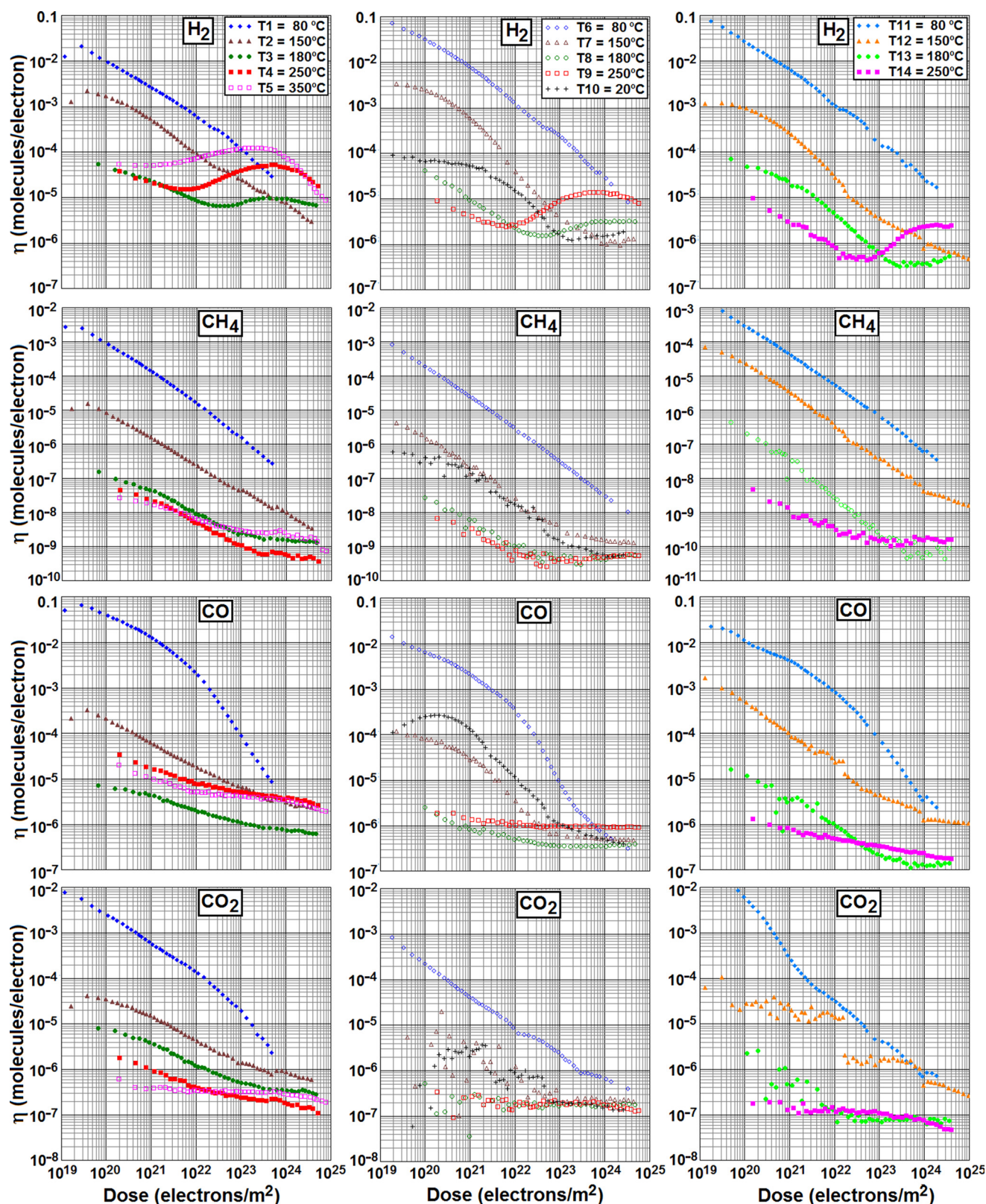
FIG. 3. (Color online) ESD yields as a function of electron dose for activated samples created by runs 1–5 (left column), runs 6–10 (middle column), and runs 11–14 (right column) for the gases (top to bottom rows) H_2, CH_4, CO, and CO_2. An index at T in the legend corresponds to the run number.

a NEG-coated vacuum chamber has been reported in Refs. 18 and 19 and is associated with hydrogen diffusion from the stainless steel substrate through the NEG coating. The higher activation temperatures (250 and 350 °C) were

not found to decrease the initial η value for the main gases in a NEG-coated chamber (H_2, CH_4, and CO), while the $\eta(H_2)$ increase was found to be higher and to begin at lower doses, which is also similar to the results reported in
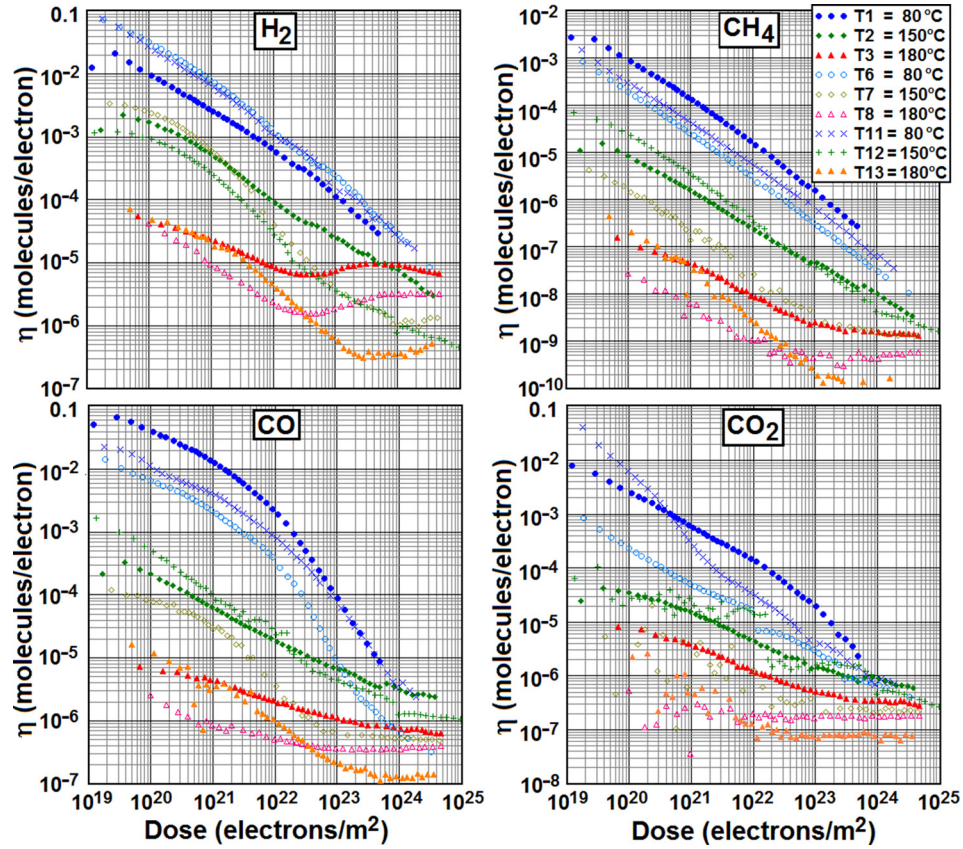
FIG. 4. (Color online) Comparison of ESD yields as a function of electron dose for samples activated at 80, 150, and 180 °C.

Refs. 18 and 19. This leads to the conclusion that the most suitable activation temperature should be between 150 and 180 °C.

For the operation of particle accelerators, it is important to understand the behavior of the NEG coating after air venting occurs. Comparison of the results from runs 1, 6, and 11 demonstrates that the memory effect of the dual film is negligible even after a short air vent, whereby the ESD yields are 3–5 orders of magnitude higher than those prior to air venting. As can be seen from Fig. 4, $\eta(D)$ graphs obtained

TABLE II. Comparison of the results for NEG films prepared at different conditions: columnar (col) and dense (den) (Ref. 18), columnar (col vf) and dense (den vf) on vacuum fired substrates (Ref. 19) and dual layer (dual).

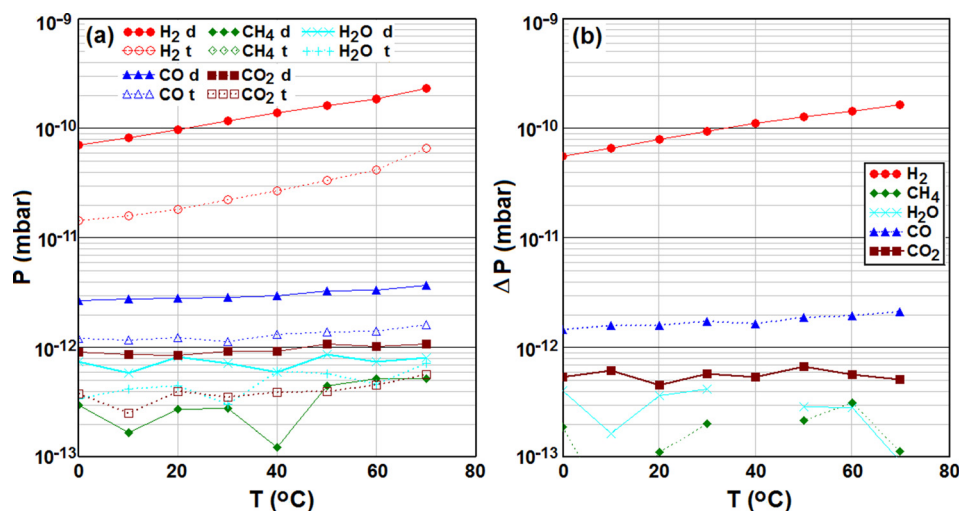| T_a (°C)	Film	Electron dose e$^-$/m^2				Electron dose e$^-$/m^2			
		10^{21}	10^{22}	10^{23}	10^{24}	10^{21}	10^{22}	10^{23}	10^{24}
		H$_2$ ESD yields				CO ESD yields			
150	Col	1×10^{-4}	2×10^{-5}	9×10^{-6}	—	2.5×10^{-5}	7×10^{-6}	5×10^{-6}	—
	Den	1.2×10^{-3}	4×10^{-4}	—	—	2×10^{-3}	4×10^{-4}	—	—
	Dual	5×10^{-4}	9×10^{-5}	2.5×10^{-5}	8×10^{-6}	6×10^{-5}	2×10^{-5}	6×10^{-6}	3×10^{-6}
	Col vf	1.5×10^{-4}	2.5×10^{-5}	4×10^{-6}	1.7×10^{-6}	3×10^{-5}	6.5×10^{-6}	2×10^{-6}	9×10^{-7}
	Den vf	3×10^{-4}	4.5×10^{-5}	9×10^{-6}	2.7×10^{-6}	1.3×10^{-4}	1.3×10^{-5}	3×10^{-6}	8×10^{-7}
180	Col	9×10^{-5}	2×10^{-5}	2×10^{-5}	—	1×10^{-5}	4.5×10^{-6}	2.5×10^{-6}	—
	Den	1×10^{-4}	3×10^{-5}	1×10^{-5}	—	2×10^{-5}	6×10^{-6}	1.5×10^{-6}	—
	Dual	2.5×10^{-5}	9×10^{-6}	8×10^{-6}	9×10^{-6}	4.5×10^{-6}	2×10^{-6}	1.2×10^{-6}	6×10^{-7}
	Col vf	3×10^{-5}	7×10^{-6}	5×10^{-6}	7×10^{-6}	3×10^{-6}	1.5×10^{-6}	7×10^{-7}	3.5×10^{-7}
	Den vf	5.5×10^{-6}	2×10^{-6}	9×10^{-7}	7×10^{-7}	3×10^{-6}	8×10^{-7}	5×10^{-7}	4×10^{-7}
250	Col	3×10^{-5}	2.3×10^{-5}	7×10^{-5}	—	6×10^{-6}	3×10^{-6}	2.4×10^{-6}	—
	Den	5×10^{-5}	2.5×10^{-5}	2×10^{-5}	—	8×10^{-6}	4.5×10^{-6}	2.4×10^{-6}	—
	Dual	2.5×10^{-5}	1.5×10^{-5}	4×10^{-5}	4×10^{-5}	1.7×10^{-5}	8×10^{-6}	5×10^{-6}	4×10^{-6}
	Col vf	7×10^{-6}	3×10^{-6}	3×10^{-6}	4.5×10^{-6}	1.7×10^{-6}	1.2×10^{-6}	6×10^{-7}	2.7×10^{-7}
	Den vf	4×10^{-6}	5×10^{-6}	7×10^{-6}	4.5×10^{-6}	7×10^{-7}	4.5×10^{-7}	3.3×10^{-7}	2.5×10^{-7}

FIG. 5. (Color online) Pressure inside NEG-coated tube (top RGA) (a) with and without electron bombardment (indicated with d and t, respectively) and (b) their pressure difference ΔP.

using the same activation temperatures are very similar. In addition, there is no degradation of the film properties.

During operation of the particle accelerator, minor vacuum accidents can occur. For example, the pressure inside the vacuum chamber can be increased to low or medium vacuum owing to an air leak or accidental gas injection. In these events, the NEG coating may be fully saturated even if the source of the accidental gas was mitigated without venting the vacuum system to air. A minor vacuum accident was simulated in run 10, when the NEG coating was fully saturated with CO at $P = 10^{-3}$ mbar for 10 min and then bombarded with electrons after a 2 h pumping with a turbomolecular pump. In this case, the ESD yields of CH_4, CO, and CO_2 behaved very similar to those in run 7 (after activation to 150 °C), and the initial $\eta(H_2)$ value was 30 times lower than that in run 7 (Fig. 3). This demonstrates that the NEG coating may not require reactivation after a minor vacuum accident owing to the so-called memory effect.

The behavior of the vacuum chambers after a minor accident was also simulated under different conditions in run 13, which induced a full saturation with CO and a 1-year long pumping followed by reactivation at 180 °C. While the long pumping duration did not affect the initial ESD yields compared to those in runs 3 and 8 (also activated at 180 °C), at doses $D > 3 \times 10^{22}$ e$^-$/m^2, the ESD yields were found to be lower for all gases. Therefore, it is advisable to maintain NEG-coated vacuum chambers under vacuum even when the NEG coating has been saturated or not activated.

The effect of vacuum chamber temperatures between 0 and 70 °C upon the pressure inside a vacuum chamber with and without electron bombardment is shown in Fig. 5. Both the pressures, without electron bombardment (defined by thermal outgassing and indicated with "t" in Fig. 5) and with electron bombardment (dynamic pressure indicated with "d"), clearly increase with temperature for H_2 and CO, and their pressure difference ΔP (defined by ESD) varies by

factors of 3 and 1.5 for H_2 and CO, respectively. For the other gases, the signal is within a noise level to make any reasonable conclusions. These results are complementary to those reported in Ref. 22, where the equilibrium H_2 pressure was studied in a vacuum chamber with a varying temperature between 100 and 250 °C.

IV. CONCLUSIONS

A dual-layer NEG coating consisting of a 0.5-μm-thick dense layer covered by a 1-μm thick columnar layer was evaluated for the first time. It was demonstrated that this dual-layer coating combined the advantages of the reduced ESD yields of a dense layer and the pumping properties of a columnar layer. Exposure to air required reactivation of the NEG coating, though reactivation was not required after minor vacuum incidents that led to full saturation. The NEG coating possessed negligible sensitivity to vacuum chamber temperatures between 0 and 70 °C, whereby ΔP varied by factors of 3 and 1.5 for H_2 and CO, respectively.

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