

Performance degradation induced by different forms of carbon contamination in superconducting rf cavities and their recovery strategies

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The performance degradation caused by carbon contaminants has become one of the significant obstacles to the long-term, high-gradient, stable operation of the SRF cavities. This paper investigates the sources and effects of different forms of carbon contamination and recovery strategies through experiments on niobium samples and a 162.5 MHz half-wave SRF cavity. Our findings reveal that adventitious carbon and oxides are the primary chemical compounds on the niobium surface, with the work function decreasing linearly as carbon content increases. Additionally, it was observed that carbides can form through the chemical deposition of residual carbon-containing gas in a vacuum under the action of argon ions. The adsorption and deposition of carbon-containing gas molecules reduce surface work function, thereby lowering the field emission onset and quench point of the cavity. However, the combination of thermal cycling and rf conditioning facilitates the desorption of adsorbed gas molecules, leading to a full recovery of cavity performance. In contrast, carbon deposition forms strong chemical bonds with the cavity surface, necessitating more intensive removal techniques. We demonstrate that plasma cleaning effectively eliminates carbon contamination and restores cavity performance. Inspired by the formation of NbC in niobium sample experiments, we propose that, during long-term SRF cavity operation, carbides primarily originate from the chemical deposition of carbon-containing gas molecules adsorbed on the surface in the presence of energy-carrying particles. These insights deepen our understanding of carbon contaminant-induced cavity performance degradation and recovery, providing a basis for selecting suitable online performance recovery methods to maintain the cavity's stable, high-gradient operation.

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I. INTRODUCTION

Superconducting radio frequency (SRF) cavities are extensively utilized in the construction of modern particle accelerators due to their high-quality factor (Q0) and higher acceleration gradient [1]. However, during long-term online operations, the field emission effect enhances over time, resulting in continuous performance deterioration. For example, following the upgrade of CEBAF to 12 GeV,

the energy has decreased by an average of 187 MeV per year [2]. Similarly, European X-Ray Free-Electron Laser Facility has experienced an energy loss of 160 MeV per year since its commissioning in 2019, and the ELBE facility at the HZDR Laboratory witnessed a decline in energy from 36 to 31 MeV between 2008 and 2012 [3,4]. To tackle this issue, several online surface treatment methods have been proposed and implemented, including rf conditioning and helium cleaning [1,5]. The rf conditioning refers specifically to the process of injecting controlled rf power into SRF cavities. This technique stimulates field emission at susceptible surface sites, thereby mitigating field-emitting protrusions (e.g., micro-protrusions and contaminants) through controlled electron discharge. Consequently, it enhances the cavity's maximum achievable accelerating gradient by suppressing field emission and multipacting phenomena. However, empirical evidence indicates that rf conditioning frequently fails to

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yield the desired results. For instance, researchers at the SNS found that rf conditioning did not lead to any performance recovery [6]. Likewise, during CEBAF operations, the average field emission onset did not exceed approximately 12 MV/m following rf conditioning [7,8], suggesting that contaminants beyond particulate matter may contribute to the field emission phenomenon. Notably, Mark Doleans *et al.* observed a minor production of CH_4 and C_2H_2 during cavity rewarming, slightly improving cavity performance [9,10]. This observation raised suspicions about the presence of carbon contaminants on the inner surface of the cavity. Subsequently, they proposed using reactive oxygen plasma for cavity cleaning, noting an enhancement in surface work function postcleaning and generating volatile gases like CO_2 and CO [10]. Validation in two horizontal test cryomodules revealed performance improvements ranging from 22% to 32% [11]. Moreover, Wu *et al.* successfully employed reactive oxygen plasma to clean a half-wave SRF cavity, observing the production of CO_2 and CO , and achieve a 29% performance enhancement at the IMP, CAS [12]. Researchers at the Fermi National Accelerator Laboratory (FNAL) developed a plasma treatment technique for 1.3 GHz nitrogen-doped cavities and demonstrated a successful reduction in field emission associated with carbon contaminants [13]. Since then, plasma cleaning techniques have been widely implemented in various SRF accelerators, yielding significant improvements in performance.

The wide application of plasma cleaning technology in SRF accelerators highlights the fact that carbon contamination is one of the main factors affecting the long-term performance degradation of SRF cavities. Current research primarily focuses on plasma cleaning for carbon contamination, with limited investigation into the sources of carbon contamination, the mechanisms of performance degradation induced by various forms of carbon contamination, and the effectiveness of corresponding recovery strategies. However, during the on-line operation of SRF cavities, there may exist many different forms of carbon contamination, such as adsorption of carbon-containing gas molecules from the residual vacuum, and chemically deposited carbon with strong bonding strength to the surface. Therefore, clarifying the sources and effects of these different forms of carbon contamination, as well as the corresponding recovery strategies, is of great significance for effectively restoring the performance of SRF cavities. In addition, it is also a key step to achieve stable and high-gradient operation of high-intensity beam accelerators.

This paper is organized as follows: Sec. II examines the chemical composition of niobium surfaces and its impact on the work function; Sec. III investigates the adsorption behavior of carbon-containing gas molecules at low temperatures and their subsequent effects; Secs. IV and V discuss the influence of carbon deposition on cavity performance, as well as potential strategies for its removal.

In Sec. VI, based on our experimental findings, we propose the hypothesis that carbides are formed through the chemical deposition of gas molecules adsorbed onto the surface of the superconducting cavity under the influence of energy-carrying particles. Finally, Sec. VII offers concluding remarks.

II. NIOBIUM SURFACE COMPOSITION ANALYSIS

A. Sample preparation and experimental procedures

Achieving a high-quality surface on SRF cavities is crucial for optimizing performance metrics such as the accelerating gradient and the unloaded quality factor. At IMP, a standardized surface processing procedure has been established, encompassing the following steps [14–16]: (i) Heavy buffered chemical polishing (BCP) involves the removal of approximately 150 μm of material to eliminate defects, particulates, oxide, and oil contaminants introduced during fabrication; (ii) High-temperature annealing at 650 $^\circ\text{C}$ for 10 h to degas hydrogen and relieve stress; (iii) Light BCP with 30 μm material to remove impurities introduced during annealing; (iv) High-pressure rinsing (HPR) with high-purity deionized water in class 100 clean rooms, followed by assembly in class 10 clean rooms. Our analysis suggests that carbon contaminants may originate from internal material sources and the adsorption of residual gases in the vacuum environment. To explore the specific sources and mechanisms of carbon contaminants' influence on cavity performance, we conducted experiments on niobium samples and a 162.5 MHz half-wave SRF cavity. The $10 \times 10 \times 1$ mm pure niobium samples and the SRF cavity underwent treatment according to the above processing steps.

This research used XPS, UPS, and Ar^+ sputtering techniques to investigate the compound compositions on the sample surfaces and establish a quantitative correlation between the chemical composition and the work function. In the experiment, we utilized a PHI-5000Versa Probes III scanning x-ray photoelectron spectroscopy (XPS, ULVAC-PHI, Inc.) instrument. The monochromatic x-ray photoelectron spectrum $\text{Al K } \alpha$ ($h\nu = 1486.6$ eV) was used as the x-ray source to excite the photoelectrons, with a base pressure of 10^{-8} Pa. The XPS setup was augmented with UPS and an argon ion gun, operating at an Ar^+ energy level of 2 keV and covering a scanning area of 3.5×3.5 mm. The XPS was first utilized to analyze the surface chemical composition of niobium samples treated using standard procedures, while UPS was employed to measure the work function. Subsequently, the niobium samples were sputtered for varying durations, with surface composition and work function measurements conducted after each sputtering cycle.

In the measurements, we took the C 1s peak with a binding energy of 284.8 eV as an example and calibrated all

relevant spectral lines to correct for the charging effect [17,18]. Meanwhile, the UPS instrument was also calibrated using a standard Ag reference sample to ensure energy scale accuracy. A bias voltage of -5 V was then applied to the sample, and the low-energy secondary electron cutoff edge and Fermi edge were measured. The work function was obtained using the following formula [19]:

$$\Phi = h\nu - (E_{\text{SE,Cutoff}} - E_{\text{Fermi}})$$

The incident photon energy ($h\nu$) was 21.2 eV (He I radiation). The secondary electron cutoff energy ($E_{\text{SE,Cutoff}}$) was determined from the intersection point between the tangent line of the secondary electron cutoff edge and the baseline in the UPS spectrum. The Fermi level position (E_{Fermi}) was identified as the horizontal coordinate value of the midpoint of the Fermi edge.

B. Distribution of niobium surface compounds

Prior investigations by our group and other institutions have established that standard-processed niobium surfaces are dominated by carbon and oxygen species. These elements react with niobium to form carbide and oxide compounds. Accordingly, this study quantitatively examines how surface work function is governed by both the concentration of C/O species and the specific chemical phases formed [20–22]. Figure 1 depicts the evolution of surface compound composition at the beginning and during sputtering. As shown in Fig. 1(a), Spectral analysis reveals that the carbon contaminants remaining on the niobium surface are mainly organic contaminants and graphite (C–C and C–O–C), similar to those remaining on the surfaces of other metal materials [23–25]. Meanwhile, it can be seen from Fig. 2(a), as the sputtering time increases, the C 1s signal intensity reaches a minimum at approximately 10 s. Subsequently, the C 1s intensity rises from 0 s–283 s, and the peak shifts to around 282.3 eV, corresponding to the binding energy of carbon in NbC. Since the C 1s show only

one peak, the peak positions and chemical compositions are easy to identify. However, as shown in Fig. 2(b), the peak intensity of O 1s exhibits a monotonic decay with sputtering time, demonstrating a progressive depletion of surface oxygen content and corresponding reduction in oxidative capacity. Through comprehensive analysis of all C 1s decomposition spectra, the evolution of carbon compositions and intensities over sputtering time can be delineated, as depicted in Fig. 1(b). Notably, the content of NbC demonstrates a rapid increase after 52 seconds. Given that the pure niobium samples used were from high-pure niobium material, the possibility of internal carbon sources was ruled out, indicating that NbC was formed gradually during the sputtering of the samples. To delve deeper into the chemical composition variations on the niobium surface during sputtering, fine analysis of Nb3d spectra was conducted at 0 s, 32 s, 52 s, and 103 s, as shown in Fig. 3. The Nb 3d spectral line fitting reveals the presence of Nb₂O₅, NbO₂ oxides and NbC on the surface at 0 s. By 32 s, the highest valence oxide Nb₂O₅ disappears, with the lower valence oxide Nb₂O occupying a dominant position. Subsequently, at 52 s, only the lower-valent Nb₂O oxides were observed. At the same time, as shown in Figs. 3(a)–3(d), NbC content increases with the decrease of higher-valence niobium oxides, which is consistent with the findings of C 1s and O 1s spectra [as shown in Figs. 2(a) and 2(b)]. This phenomenon primarily stems from the competitive relationship between niobium oxide and carbide formation, where niobium has a stronger oxygen affinity compared to carbon, which prevents the formation of NbC under oxygen-rich conditions. The carbide mainly originates from the interaction of low-energy argon ions with the residual carbon-containing gas molecules in the vacuum, promoting the deposition of residual carbon on the surface of niobium, and ultimately the formation of NbC [17]. Inspired by the formation of NbC in the small sample experiment, we consider that in the operation of the SRF cavity, there are various energy-carrying particles such as accelerating particles, secondary electrons, and field

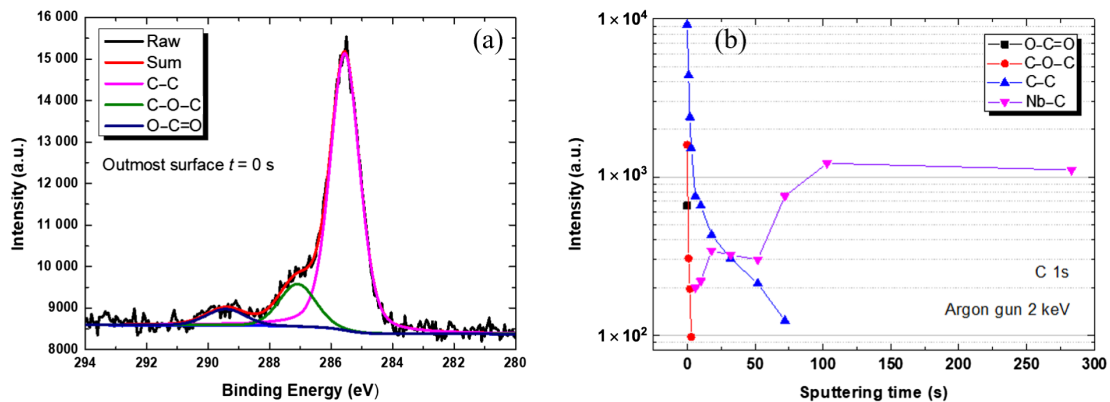


FIG. 1. XPS analysis of the chemical composition of niobium surface (a) the surface composition before Ar⁺ sputtering, (b) the surface compositional analysis during Ar⁺ sputtering.

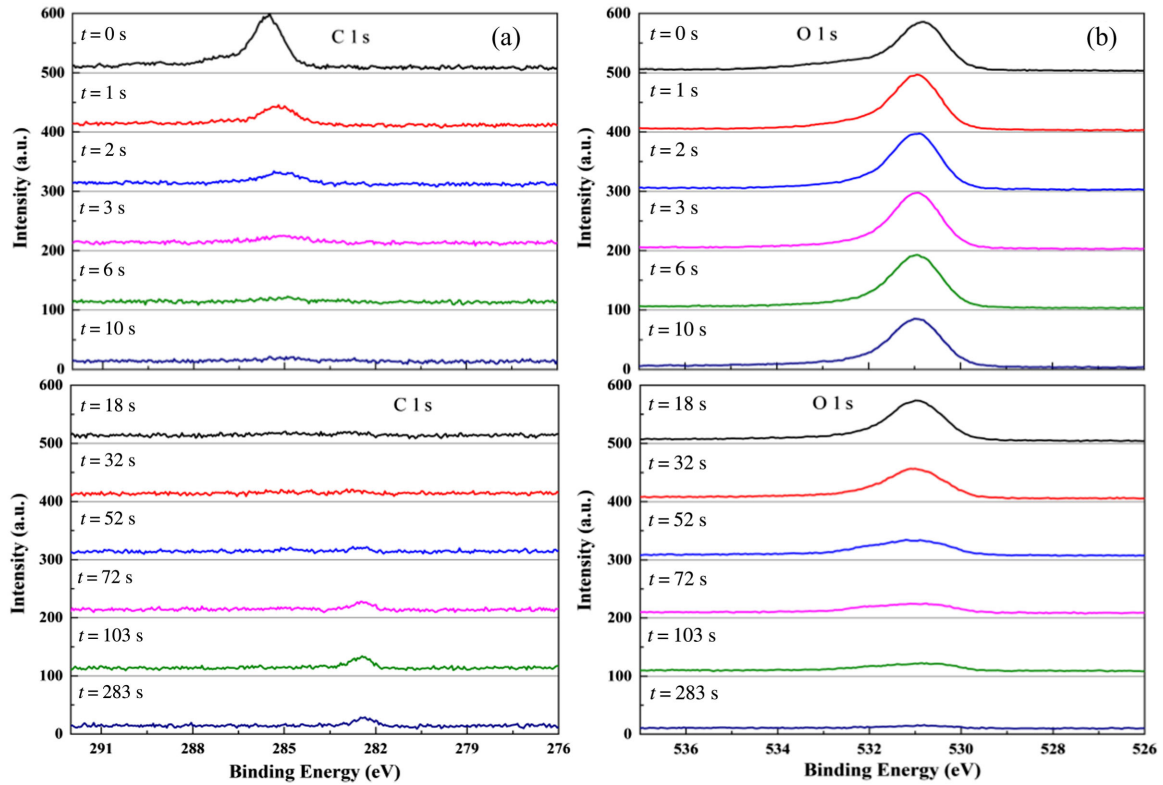


FIG. 2. The variation of (a) carbon and (b) oxygen elements with sputtering time.

emission electrons, and so on. If some carbon-containing gas molecules are adsorbed in the SRF cavity, these energy-carrying particles can interact with them, thus providing some energy for their deposition. Therefore, we put forward a conjecture on the origin of carbide in SRF cavities in Sec. VI in conjunction with our experience of operating SRF cavities.

C. Effect of carbides and oxides on the work function

Since the change in work function is closely related to surface composition, and work function directly affects the onset of field emission, this section mainly studies the correspondence between work function and surface composition. Figure 4 illustrates the surface chemical composition and work function evolution over sputtering time. The δ parameter quantitatively describes the oxidation state of niobium, where higher δ values correlate with lower oxidation states. For instance, $\delta = 1$ corresponds to Nb^{4+} , while $\delta = 4$ indicates Nb^+ . Notably, when δ increases from 0.8 to 1.8, the carbon content decreases from 30% to 5%, concomitant with a work function increase from 3.75 to 4.41 eV within the 0–6 s. Additionally, the δ value, indicative of niobium's oxidation valence, increases from 0.8 to around 1.8, implying a direct reduction in surface work function due to carbon presence. In 6–72 s, the work function decreases from 4.41 to 4.07 eV. Meanwhile, δ rises from 1.87 to 4.48, with carbon content exhibiting minor

fluctuations within the 3% to 5% range. This trend highlights that as the oxidation valence of niobium decreases, the work function is also decreased, suggesting that increasing the chemical valence of the surface oxide promotes an increase in the work function. In Fig. 5(a), the Nb 3d spectral analysis at 6 s shows that the predominant surface components are NbC, NbO_2 , and Nb_2O_5 . Notably, the highest valence oxides reside in the outermost layer, while the lower valence oxides are concentrated in the innermost layer. Consequently, during the 0–6 s interval, the work function is primarily influenced by the outermost Nb_2O_5 and adventitious carbon [23], with the lower valence oxides in the deeper layers exhibiting negligible impact on the work function. At the same time, since the outermost oxide changes very little within 0–6 s, we can directly relate the carbon content to the work function. As shown in Fig. 5(b), the work function decreases linearly with the increase in the C 1s content, indicating that there is a linear correlation between the work function and the carbon content.

As a result, the compounds on the surface of niobium are mainly oxides and adventitious carbon, and the work function decreases continuously with the increase of carbon. Enhancing the presence of high-valence oxides on the surface while reducing carbon content improves the work function, thereby improving the field emission onset and operational performance. Moreover, this suggests that residual carbon remains on the inner surfaces of the cavities

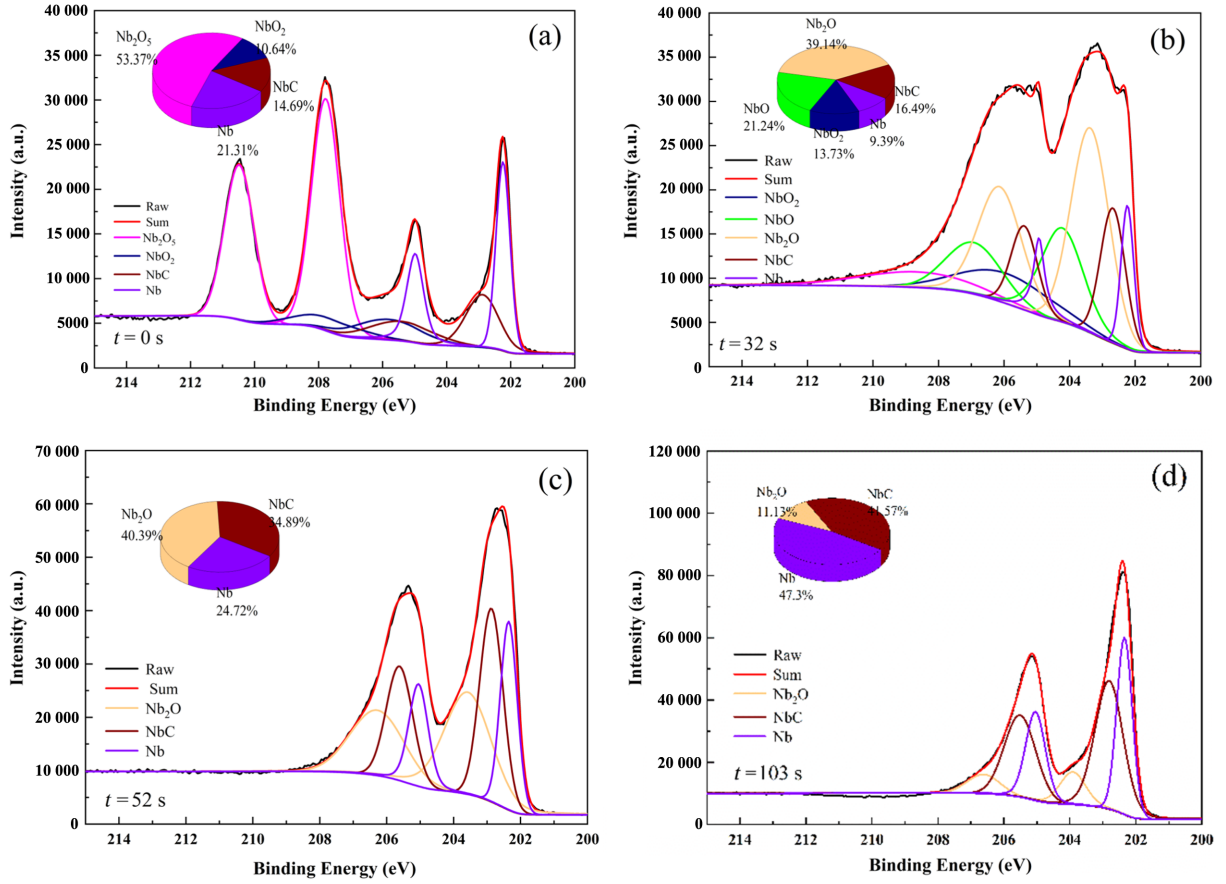


FIG. 3. The change of niobium oxide and NbC with different sputtering time.

after standard process treatments [21,22,26]. Operational experience with different superconducting cavities has shown that cavities treated with standard processes and then subjected to online plasma cleaning prior to initial operation exhibit significantly improved performance, indicating that residual carbon contamination also has a significant impact on the initial surface. In addition, the

formation of NbC during argon ion sputtering primarily originates from the energy generated by the argon ions bombardment, facilitating surface carbide deposition. Similarly, when the SRF cavity is cooled to approximately 2 K, gas molecules tend to adsorb on its inner surface despite continuous vacuum pumping, leading to the accumulation of residual carbon-containing gases. These

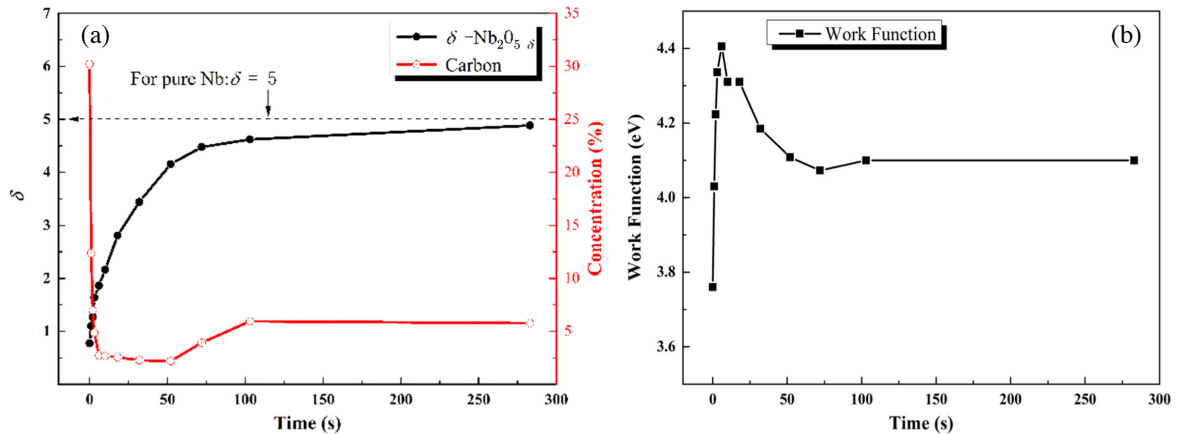


FIG. 4. Relationship between niobium oxide, carbon, work function, and sputtering time.

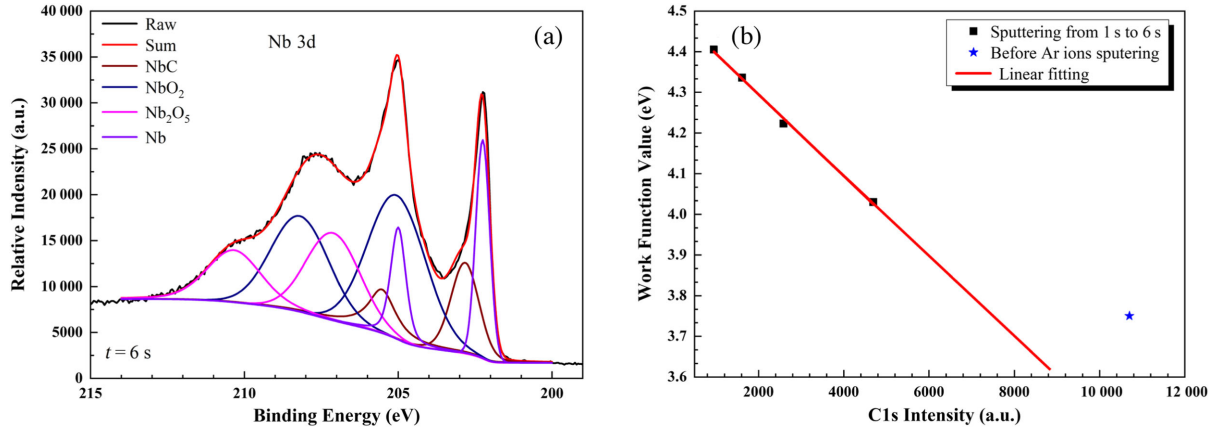


FIG. 5. Chemical composition and work function analysis of niobium surfaces at a sputtering time of 6 s, (a) Deconvolution analysis of Nb 3d, (b) Variation of work function with intensity of C 1s in 0–6 s of sputtering.

adsorbed carbon-containing gas molecules may then form carbide contaminants under the influence of high-energy particles (e.g., accelerated ions and dark currents).

III. EFFECT OF CRYOGENIC ADSORBED CARBON CONTAMINATION ON CAVITIES

A 162.5 MHz half-wave type SRF cavity with an optimized beta of 0.15 was used for contamination studies. Zhang *et al.* investigated the multipacting effects in this cavity and revealed a potential multipacting zone occurring between 15 and 19 MV/m of the maximum surface electric field [27]. Consequently, a 2–5 min rf conditioning was routinely implemented to mitigate multipacting before commencing data collection for Q_0 and x-ray dose assessments. The vertical test outcomes of the standardized half-wave SRF cavity at 4 K are depicted in Fig. 7.

A. Experimental procedure for cryogenic adsorption

The study of cryogenic adsorption of hydrocarbon contamination on the inner surface of the cavity was performed on the vertical test stand at IMP, where methane was used as the hydrocarbon contaminant source. Figure 6 shows the schematic of the experimental setup. The experimental procedures are as follows: (i) Test the cavity at 4 K before the contamination as baseline; (ii) Warm up the cavity to room temperature with valve III closed, and pump the cavity to about 2.0×10^{-6} Pa, close valve I to isolate the pumping station, then open valve III, inject the methane gas to the cavity about 11 mL followed by closing valve II, the gas pressure inside the cavity was approximately 9.2 Pa (Note: 9.2 Pa is an arbitrarily chosen value.); (iii) Cool the cavity to 4 K while activating the vacuum pump to achieve an ultimate pressure of 1.9×10^{-6} Pa. The vacuum pressure decreased within the cavity from 2×10^{-6} Pa (at room temperature) to 1.9×10^{-6} Pa (at 4 K), indicating that methane gas was adsorbed onto the inner

surface of the cavity because of the cryogenic effects of the material.

B. Cavity performance testing after methane adsorption

As shown in Fig. 7, the correlations between Q_0 , x-ray signals, and E_{peak} in the half-wave resonator (HWR) cavity evolve after methane adsorption, carbon deposition, and plasma treatment. The following section provides a detailed analysis of the field emission onset and quench points revealed in this figure. Following 3-h adsorption at 4 K, a vertical test was conducted on the methane-contaminated cavity. Figure 8 shows the test result of the FE onset and

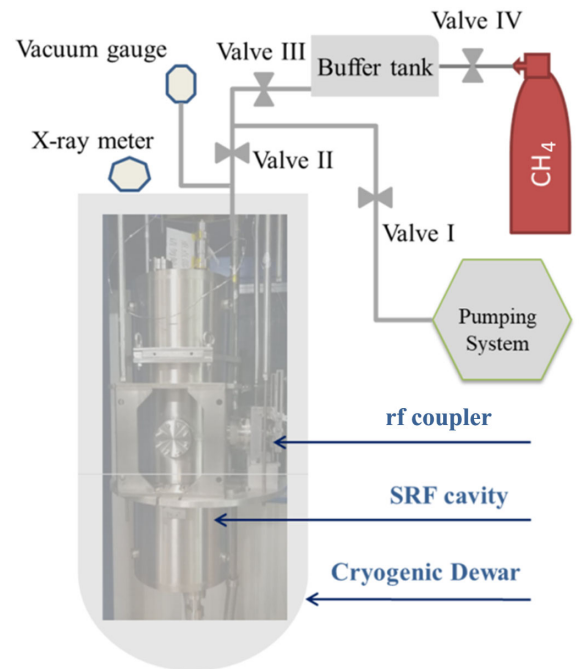


FIG. 6. Vertical test stand and methane feeding system for SRF cavity.

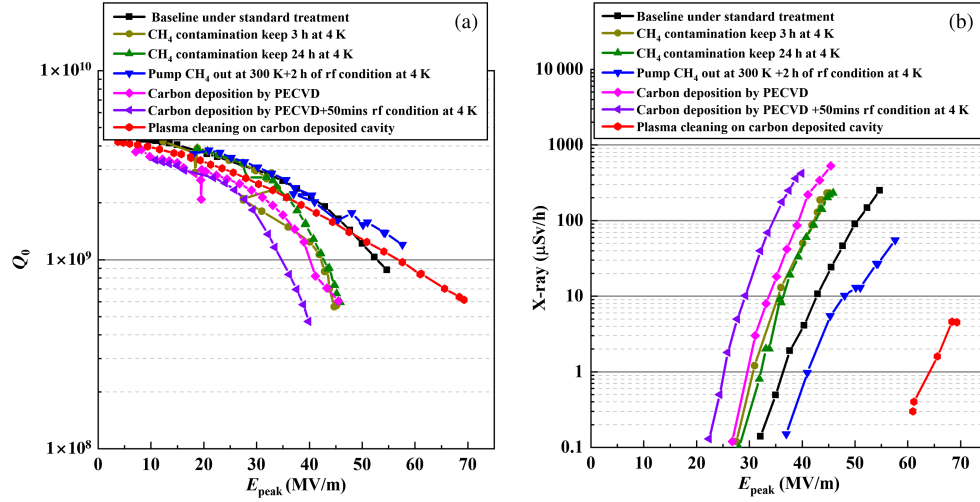


FIG. 7. Vertical measurement results for carbon adsorption, deposition, and plasma cleaning in the HWR cavity: (a) Dependence of Q_0 on E_{peak} ; (b) Dependence of x-ray on E_{peak} .

quench point. As one can see, the field emission inside the cavity deteriorated, with the FE onset decreasing from 32.4 to 28.1 MV/m and the quenching field falling from 54.7 to 45.5 MV/m, thereby confirming hydrocarbons as one of the sources of field emission [28]. During the test, when the field emission occurred, the *vacuum pressure* increased from 1.9×10^{-6} Pa to 1.0×10^{-5} Pa, indicating methane desorption from the cryogenic surface. Subsequently, valves I and II were opened for 24 h to evacuate all desorbed methane gas. Following this evacuation, the cavity's vacuum was restored to 1.0×10^{-6} Pa. Valve II was then closed, and a second test was performed at 4 K. It is found that the performance of the cavity did not exhibit improvement; field emission persisted, and the cavity's vacuum level stabilized at 1.0×10^{-6} Pa. This observation

suggests that a portion of the adsorbed methane did not desorb, leading to the persistence of field emission.

C. Elimination of adsorbed carbon contaminants

In order to eliminate hydrocarbon contaminants adsorbed to the inner surface of the cavity at cryogenic temperatures, a thermal cycling procedure was implemented. The cavity was cycled to 300 K, evacuated to 1.0×10^{-6} Pa, and cooled to 4 K for testing. During the tests, it was found that the cavity suffered from a severe multipacting barrier that could not be overcome by the 10-min rf conditioning alone. To address this issue, an additional 2-h rf conditioning was used to eliminate the multipacting barrier. The test results are shown in Fig. 8, demonstrating that the combination of thermal cycling and rf conditioning effectively restored the performance degradation caused by the cryogenic adsorption of methane. Moreover, after an extended 2-h rf conditioning process, the cavity exhibited improvements in both the field emission onset and quenching point, with enhancements of approximately 15% and 5%, respectively, compared to the baseline results.

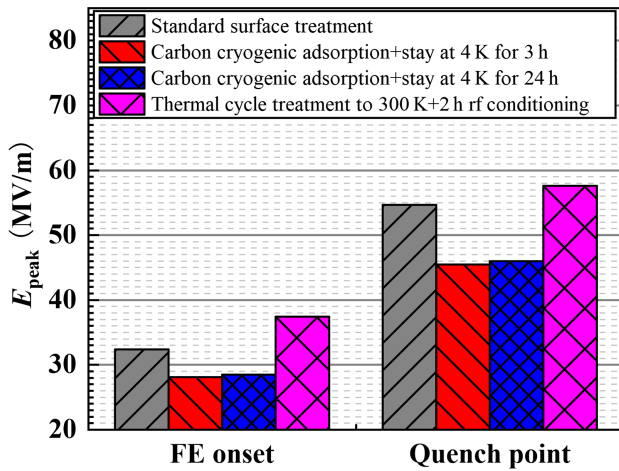


FIG. 8. Vertical test results of SRF cavity under condition of carbon cryogenic adsorption and removing by thermal cycle procedure.

IV. EFFECTS OF CHEMICALLY DEPOSITED CARBON CONTAMINATION ON CAVITIES

A. Chemical deposition of carbon contamination

In methane adsorption experiments of the SRF cavities, we discovered that the performance of the cavity can be completely restored through combined treatment with thermal cycling and rf conditioning. This finding suggests that adsorbed carbon contamination is not the primary cause of performance degradation in cavities during long-term operation. In addition to adsorption, carbon-containing gas molecules might also deposit on the inner surface of

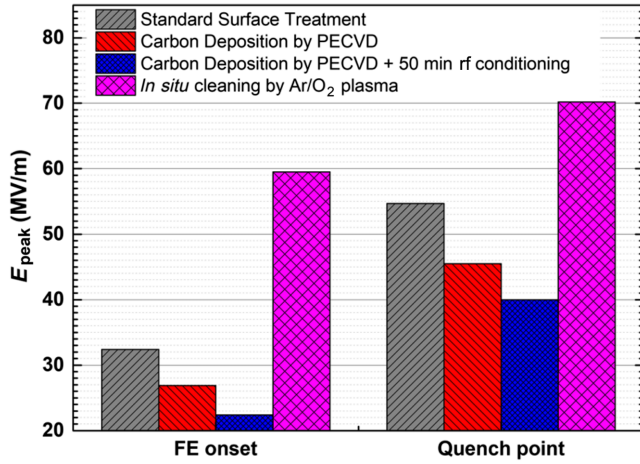


FIG. 9. The effects of carbon deposition contamination and *in situ* plasma cleaning on SRF cavity.

the cavity. Deposited carbon contamination forms stronger chemical bonds compared to adsorbed carbon, rendering it more challenging to eliminate through thermal cycling.

Understanding how carbon is deposited on niobium surfaces is crucial for directly studying the impact of carbon contamination on SRF cavity performance. Based on the half-wave SRF cavity plasma ignition, control, and monitoring techniques developed by our team in the previous study, we conducted carbon contaminant deposition experiments using plasma-enhanced chemical vapor deposition (PECVD) method. Plasma-enhanced chemical vapor deposition technique is widely used to deposit thin films on material surfaces to improve surface properties. This technique primarily utilizes high-energy electrons in the plasma to crack the reacting gas, generating highly active ground-state or deposited atoms that can be deposited to form thin films [29–31].

In our experiments, we utilized the PECVD technique to deposit carbon contaminants in the HWR cavity at room temperature. An Ar/CH₄ mixture gas rf glow discharge was employed, with a methane gas volume ratio of 2.5%,

gas pressure of 0.8 Pa, power of 80 W, and a total deposition time of 5 min. Then, the rf power supply and inlet valve were turned off, and the SRF cavity was rapidly evacuated to 1.2×10^{-6} Pa using a vacuum pump to mitigate the effects of residual gas adsorption. Finally, the cavity was cooled to a cryogenic temperature of 4 K for testing.

B. Performance testing of carbon deposition cavities

Figure 9 shows the results of the FE onset and quench point for the cavities after carbon deposition. The results indicate the performance of the SRF cavities decreases dramatically after carbon deposition, with the FE onset decreasing from 32.8 to 27.5 MV/m and the quench point decreasing from 54.7 to 45.5 MV/m. In order to further study the changes in the surface composition of niobium after methane cracking deposition, we conducted carbon deposition experiments similar to those in the cavity on the samples. For carbon deposition studies, samples were exposed to Ar/CH₄ plasma (2.5 vol% CH₄, 80 W, 15 min). XPS analysis of the Nb 3d fine spectra [Fig. 10(a)] revealed the formation of multiple surface species, including NbH, NbC, nonstoichiometric NbC_x ($x < 1$), Nb–C–O, and Nb₂O₅. The observed Nb–C–O phase resulted from partial oxidation of NbC, while carbon vacancies led to the formation of defective NbC_x. UPS measurements [Fig. 10(b)] demonstrated a significant reduction in work function from 4.4 eV (pure Nb) to 2.5 eV following carbon deposition. This clearly demonstrates that the deposition of carbon contaminant reduces the surface work function, thereby enhancing field emission, which in turn causes heat accumulation and reduces the quenching field.

In addition, it is worth noting that the multipacting effect reappeared at 16–19 MV/m, resulting in a sharp decline in Q_0 (as shown in Fig. 7), which could not be resolved with a mere 10-min rf conditioning session. To mitigate both multipacting and field emission (FE), an additional 50 min of rf conditioning was performed. However, as shown in

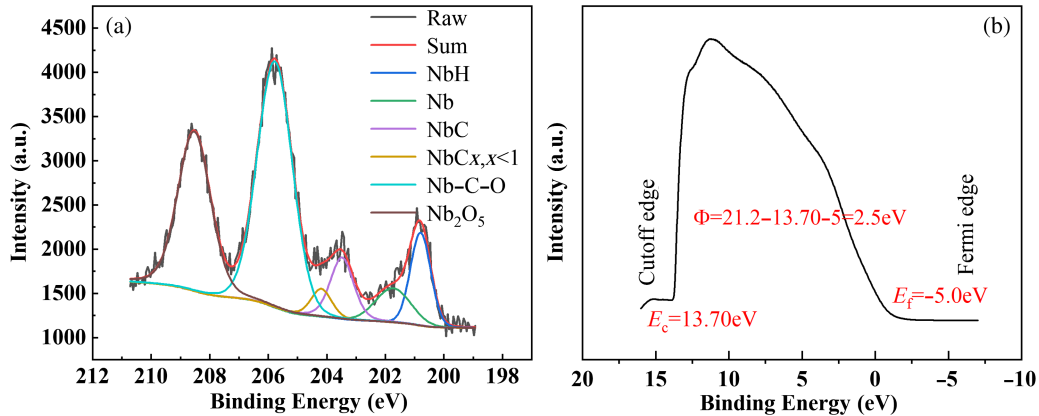


FIG. 10. (a) Fine spectra and (b) work function changes of Ar/CH₄ deposition for 15 min samples.

Fig. 7, this led to a further deterioration in the cavity's performance. The vertical test again found that the field emission onset and quench point decreased to 22.5 and 40.2 MV/m. Hence, when HWR cavities are contaminated with hydrocarbons, an extended rf conditioning process can effectively combat the multipacting barrier but may exacerbate the field emission effect. These behaviors can be explained by the migration of contaminants within the cavity. When PECVD is used to deposit carbon in the cavity, these carbon contaminants may be deposited at all locations inside the cavity, and it is known from previous simulations of the HWR cavity that the multipacting effect occurs mainly at both ends of the cavity [27]. Hence, the contaminants in these positions increase the surface secondary electron emission coefficient, aggravating the multiplication barrier. However, a 50-min rf conditioning prompts the migration of carbon contamination from the multipacting-prone zones to regions with stronger electric fields, eliminating the multipacting effect while exacerbating the field emission effect by further reducing the surface work function.

V. REMOVAL OF CARBON CONTAMINANTS BY *IN SITU* PLASMA CLEANING

A. Performance testing of plasma-cleaned cavities

Plasma cleaning is widely employed in SRF accelerators to effectively eliminate hydrocarbon contaminants from surfaces [32–35]. In this study, Ar/O₂ plasma was utilized to remove carbon contamination deposited on the inner surface of the half-wave SRF cavity. This technique primarily uses active oxygen atoms to react with carbon, producing volatile CO₂ and CO, and thereby eliminating contaminants. To mitigate thermal loading on superconducting cavities and cryogenic systems caused by sustained ion bombardment from nonpulsed plasma, we maintain plasma operation in pulsed mode. This approach prevents localized heat accumulation at cavity walls while preserving plasma processing efficacy. The cleaning process involved an oxygen volume ratio of 3%, a total pressure ranging from 0.6 to 0.9 Pa, radiofrequency forward power between 80 and 120 W, and the operation of plasma in a “pulsed mode” with 10-s pulses separated by 2-min intervals, totaling a cleaning duration of approximately 90 min. The vertical test results of the cleaned cavity were shown in Fig. 9, demonstrating a significant enhancement compared to the baseline results, with an 83% increase in the field emission onset (from 32.5 to 59.5 MV/m) and a 28% rise in the quench point (from 54.5 to 70.2 MV/m). In addition, the x-ray radiation dose from emitted electrons drastically decreased from several hundred $\mu\text{Sv/h}$ to 4.5 $\mu\text{Sv/h}$, as illustrated in Fig. 11. Based on our team's previous research findings, it can be deduced that the deposited carbon reacted chemically with oxygen plasma to generate volatile CO and CO₂, thereby effectively

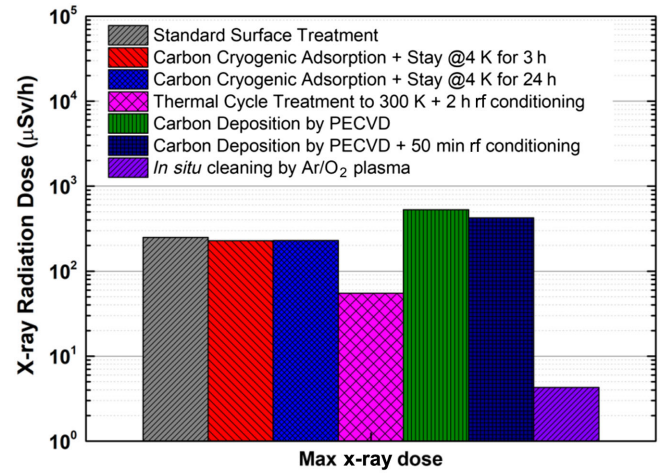


FIG. 11. The x-ray dose of half-wave SRF cavity under different treatments.

eliminating carbon contamination [12]. This reduction indicates that the deposited carbide contaminants have a stronger binding force to the surface and can be removed using reactive oxygen plasma. It also confirms that the carbides in the cavity are mainly from chemical deposition of carbon-containing gas molecules remaining in the vacuum environment after the injection of the methane gas.

B. Evolution of surface composition and work function after plasma cleaning

From previous experimental analysis, we found that the surface work function decreases linearly with the increase of carbon contamination, and the reactive oxygen plasma can effectively improve the performance of the cavity. However, because of the cavity's large volume and complex structure, it is impossible to directly determine the changes in surface composition and work function. Meanwhile, in order to compare with the niobium samples and the HWR cavity deposited with Ar/CH₄ plasma, we cleaned the carbon-deposited samples using an inductively coupled plasma (ICP) source. The ICP source was driven by a 13.56 MHz rf power source, with a power range of 10–300 W and an oxygen ratio of 3%. By adjusting the discharge parameters of the ICP source, it is possible to generate plasma with electron density and temperature closely approximating those inside the cavity—specifically, with electron densities on the order of 10^{15} – 10^{17} m⁻³ and electron temperatures between 1 and 3 eV [12]. Although the absolute values are not identical, these parameters predominantly affect reaction rates rather than altering the fundamental reaction mechanisms. Therefore, we conclude that the chemical processes observed in ICP-based experiments can adequately represent those occurring within the cavity.

By adjusting the discharge parameters of the ICP source, the electron density and temperature can be maintained

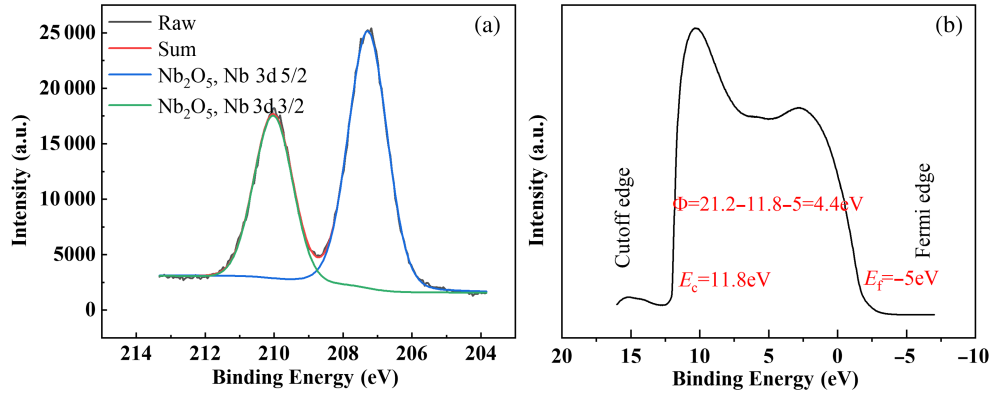


FIG. 12. (a) Fine spectrum and (b) work function changes after 3 h of Ar/O₂ plasma cleaning of the carbon deposition sample in Fig. 10.

within the ranges of 10^{16} – 10^{17} m^{-3} and 1–10 eV, respectively, to align them as closely as possible with the characteristics of the plasma in the HWR cavity. This ensures consistency in the cleaning of both the sample and the HWR cavity. Thus, the sample cleaning can reflect the interaction of the plasma with the niobium surface during *in situ* cleaning in the SRF cavity.

We conducted a 3-h Ar/O₂ (3%) plasma cleaning (3 vol% O₂, 80 W, 3 h) on the carbon deposition sample in Fig. 10, and the results are shown in Fig. 12. XPS and UPS analyses [Figs. 12(a) and 12(b)] demonstrated complete removal of surface NbC species along with oxidation of the niobium surface to Nb₂O₅, accompanied by improvement of the work function to 4.4 eV. These findings provide direct experimental evidence linking carbon contamination to HWR cavity performance degradation, while demonstrating that plasma cleaning effectively reverses these effects through carbon removal and surface oxide regeneration. The quantitative agreement between these surface science measurements and our previous cavity performance data establishes a definitive correlation between surface chemical state and superconducting rf properties, offering important insights for cavity processing and performance optimization. By combining the samples and cavity cleaning experiments, we can find that carbon contamination still exists on the surface after the standard surface process. Still, the plasma can completely remove carbon contamination from the surface, leaving only Nb₂O₅, which is the reason why the performance of the cavity is better than the baseline level after plasma cleaning.

VI. SPECULATIONS ON THE ORIGIN OF CARBON CONTAMINANTS IN SRF CAVITIES

Through small sample experiments, we have observed that NbC can form during Ar⁺ sputtering. This is attributed to the decomposition and subsequent deposition of residual carbon-containing gas molecules within the vacuum chamber, induced by the action of Ar⁺. However, during the

operation of SRF cavities, where the temperature is maintained at approximately 2 K, the surface may adsorb residual carbon-containing gas molecules. Additionally, various energy-carrying particles, such as beam losses and field emission electrons, are present within the SRF cavity. The interaction between these particles and the adsorbed gas molecules on the cavity surface can lead to the decomposition and redeposition of the carbon-containing gas molecules. As a result, the deposited carbon may arise from a chemical transformation of the adsorbed carbon-containing gas molecules, transitioning from physical adsorption to chemical deposition with a strong bond formation, facilitated by the presence of energy-carrying particles.

To validate this hypothesis, we are designing and constructing an online research platform for evaluating the performance of SRF materials. This platform is capable of simulating the extreme conditions encountered by SRF cavities, including ultralow temperatures, strong electric fields, high vacuum, and ionic radiation environments. We will test this hypothesis through ion irradiation of carbon-containing gas molecules adsorbed at low temperatures, followed by an analysis of the changes in the sample surface both before and after adsorption and irradiation.

VII. CONCLUSION

In this paper, the effects of different forms of carbon contamination on cavity performance and recovery strategies were investigated using niobium samples and 162.5 MHz half-wave SRF cavities. Analysis of the niobium samples revealed that the predominant surface compounds are carbides and oxides, with the surface work function exhibiting a linear decrease as the carbide content increases. Additionally, it was observed that residual carbon-containing gas molecules in the vacuum chamber undergo chemical deposition under the influence of argon ions. To further explore the effects of different forms of carbon contamination on cavity performance, we conducted methane adsorption and deposition experiments.

Cryogenic adsorption experiments at 4 K indicated that methane adsorption lowers the work function, thereby reducing the field emission onset and quench points of the cavity. However, thermal cycling and rf conditioning were shown to fully recover the cavity's performance. In contrast, carbide deposition led to a reduction in the surface work function, which further lowered the field emission onset and quench point. Moreover, rf conditioning after carbide deposition may cause contaminant migration, thereby exacerbating the deterioration of cavity performance. Subsequently, a reactive oxygen plasma cleaning technique was employed to eliminate carbon contamination within the cavity. This process successfully removed surface carbon contaminations, leading to an increase in the work function, and consequently, the field emission onset and quench points surpassed baseline levels, allowing for complete recovery of cavity performance. Finally, based on the formation of NbC under the influence of argon ions in niobium sample experiments, we propose that the carbides found in long-term operation of SRF cavities predominantly originate from the chemical deposition of carbon-containing gas molecules adsorbed on the surface in the presence of energy-carrying particles. These findings provide a deeper understanding of the origins of carbon contamination and its impact on cavity performance during extended operational periods. Moreover, these results offer valuable insights for the selection of appropriate *in situ* performance recovery techniques.

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DATA AVAILABILITY

The data are not publicly available. The data are available from the authors upon reasonable request.

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- [1] H. Padamsee, 50 years of success for SRF accelerators—A review, *Supercond. Sci. Technol.* **30**, 053003 (2017).
 - [2] R.-L. Geng, A. Freyberger, and R. Rimmer, Understanding and mitigation of field emission in CEBAF SRF linacs, in *Proceedings of the 10th International Particle Accelerator Conference, IPAC-2019, Melbourne, Australia* (JACoW, Geneva, Switzerland, 2019).

- [3] N. Walker, Experience with field emitters at the European XFEL, in *Proceedings of the TTC 2021 Meeting, TESLA Technology Collaboration, Hamburg, Virtual Meeting* (2021).
- [4] A. Arnold, A. Büchner, H. Büttig, M. Freitag, U. Lehnert, M. Doleans *et al.*, *15 Years of CW SRF Operation at ELBE* (TTC, 2018), https://indico.triumf.ca/event/288/contributions/3652/attachments/2790/3422/Ariel_Talk_AA_V1.pdf.
- [5] C.-H. Lo *et al.*, Vertical test of a 500-MHz srf cavity with a closed-loop cryogenic helium system, *IEEE Trans. Appl. Supercond.* **29**, 1 (2019).
- [6] S.-H. Kim *et al.*, Overview of ten-year operation of the superconducting linear accelerator at the Spallation Neutron Source, *Nucl. Instrum. Methods Phys. Res., Sect. A* **852**, 20 (2017).
- [7] R. L. Geng, A. Freyberger, and R. A. Rimmer, Understanding and mitigation of field emission in CEBAF SRF linacs, No. JLAB-ACC-19-2988; DOE/OR/23177-4740, Thomas Jefferson National Accelerator Facility (TJNAF), Newport News, VA (United States), 2019.
- [8] Y. Khopkar, G. Denbeaux, and V. Jindal, Root causes of field emitters in SRF cavities placed in CEBAF tunnel, in *Proceedings of the 7th International Particle Accelerator Conference, IPAC-2016, Busan, Korea* (JACoW, Geneva, Switzerland, 2016), p. 90483M, <https://inspirehep.net/literature/1470446>.
- [9] M. Doleans, Ignition and monitoring technique for plasma processing of multicell superconducting radio-frequency cavities, *J. Appl. Phys.* **120**, 243301 (2016).
- [10] S.-H. Kim, M. Crofford, M. Doleans, J. Saunders, and J. Mammoser, R&D status for in-situ plasma surface cleaning of SRF cavities at SNS, in *Proceedings of 2011 Particle Accelerator Conference, New York, NY, USA* (2011).
- [11] M. Doleans *et al.*, *In-situ* plasma processing to increase the accelerating gradients of superconducting radio-frequency cavities, *Nucl. Instrum. Methods Phys. Res., Sect. A* **812**, 50 (2016).
- [12] A. Wu *et al.*, *In-situ* plasma cleaning to decrease the field emission effect of half-wave superconducting radio-frequency cavities, *Nucl. Instrum. Methods Phys. Res., Sect. A* **905**, 61 (2018).
- [13] B. Giaccone, M. Martinello, P. Berrutti, O. Melnychuk, D. A. Sergatskov, A. Grassellino, D. Gonnella, M. Ross, M. Doleans, and J. F. Zasadzinski, Field emission mitigation studies in the SLAC Linac Coherent Light Source II superconducting rf cavities via *in situ* plasma processing, *Phys. Rev. Accel. Beams* **24**, 022002 (2021).
- [14] A. D. Wu *et al.*, The cryostat results of carbon contamination and plasma cleaning for the field emission on the SRF cavity (2019).
- [15] M. Yu *et al.*, The oxidation behaviors of high-purity niobium for superconducting radio-frequency cavity application in vacuum heat treatment, *Vacuum* **203**, 111258 (2022).
- [16] T. Jiang, Y. Huang, S. Zhang, L. Liu, P. Xiong, C. Li, H. Guo, W. Yue, S. Zhang, and Y. He, Design and test result of a superconducting double-spoke cavity, *Nucl. Eng. Technol.* **51**, 877 (2019).

- [17] J. Landoulsi, M.J. Genet, S. Fleith, Y. Touré, I. Liascukienė, C. Méthivier, and P.G. Rouxhet, Organic adlayer on inorganic materials: XPS analysis selectivity to cope with adventitious contamination, *Appl. Surf. Sci.* **383**, 71 (2016).
- [18] E. Korin, N. Froumin, and S. Cohen, Surface analysis of nanocomplexes by X-ray Photoelectron Spectroscopy (XPS), *ACS Biomater. Sci. Eng.* **3**, 882 (2017).
- [19] R. Pandiyan, Z. Oulad Elhmaidi, Z. Sekkat, M. Abd-lefdil, and M. A. El Khakani, Reconstructing the energy band electronic structure of pulsed laser deposited CZTS thin films intended for solar cell absorber applications, *Appl. Surf. Sci.* **396**, 1562 (2017).
- [20] Z. Zhang *et al.*, The mechanism study of mixed Ar/O₂ plasma-cleaning treatment on niobium surface for work function improvement, *Appl. Surf. Sci.* **475**, 143 (2019).
- [21] A. Daccà, G. Gemme, L. Mattera, and R. Parodi, XPS analysis of the surface composition of niobium for superconducting RF cavities, *Appl. Surf. Sci.* **126**, 219 (1998).
- [22] A. D. Batchelor, D. N. Leonard, P. E. Russell, F. A. Stevie, D. P. Griffis, and G. R. Myneni, TEM and SIMS analysis of (100), (110), and (111) single crystal niobium, *AIP Conf. Proc.* **927**, 72 (2007).
- [23] H. Piao and N. S. McIntyre, Adventitious carbon growth on aluminium and gold–aluminium alloy surfaces, *Surf. Interface Anal.* **33**, 591 (2002).
- [24] M. C. Biesinger, Accessing the robustness of adventitious carbon for charge referencing (correction) purposes in XPS analysis: Insights from a multi-user facility data review, *Appl. Surf. Sci.* **597**, 153681 (2022).
- [25] L. H. Grey, H.-Y. Nie, and M. C. Biesinger, Defining the nature of adventitious carbon and improving its merit as a charge correction reference for XPS, *Appl. Surf. Sci.* **653**, 159319 (2024).
- [26] T. Hryniewicz, K. Rokosz, and H. R. Z. Sandim, SEM/EDX and XPS studies of niobium after electropolishing, *Appl. Surf. Sci.* **263**, 357 (2012).
- [27] C. Zhang, S.-H. Zhang, Y. He, W.-M. Yue, and W. Chang, Multipacting analysis for half wave resonators in the China ADS, *Chin. Phys. C* **39**, 117002 (2015).
- [28] C. N. Stewart and G. Ehrlich, Dynamics of activated chemisorption: Methane on rhodium, *J. Chem. Phys.* **62**, 4672 (1975).
- [29] M. Meyyappan, L. Delzeit, A. Cassell, and D. Hash, Carbon nanotube growth by PECVD: A review, *Plasma Sources Sci. Technol.* **12**, 205 (2003).
- [30] H. Takatsuka, M. Noda, Y. Yonekura, Y. Takeuchi, and Y. Yamauchi, Development of high efficiency large area silicon thin film modules using VHF-PECVD, *Solar Energy* **77**, 951 (2004).
- [31] N. Nelson, R. T. Rakowski, J. Franks, P. Woolliams, P. Weaver, and B. J. Jones, The effect of substrate geometry and surface orientation on the film structure of DLC deposited using PECVD, *Surf. Coat. Technol.* **254**, 73 (2014).
- [32] M. Doleans, Ignition and monitoring technique for plasma processing of multicell superconducting radio-frequency cavities, *J. Appl. Phys.* **120**, 243301 (2016).
- [33] P. V. Tyagi *et al.*, Improving the work function of the niobium surface of SRF cavities by plasma processing, *Appl. Surf. Sci.* **369**, 29 (2016).
- [34] M. Doleans *et al.*, *In-situ* plasma processing to increase the accelerating gradients of superconducting radio-frequency cavities, *Nucl. Instrum. Methods Phys. Res., Sect. A* **812**, 50 (2016).
- [35] S. Ahmed and J. D. Mammoser, Microwave induced plasma discharge in multi-cell superconducting radio-frequency cavity, *Rev. Sci. Instrum.* **86**, 073303 (2015).