

MEASUREMENT OF THE HIGH-FIELD Q-DROP IN A LARGE-GRAIN NIOBIUM CAVITY FOR DIFFERENT OXIDATION PROCESSES*

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Abstract

In this contribution, we present the results from a series of RF tests at 1.7 K and 2.0 K on a single-cell cavity made of high-purity large (with area of the order of few cm²) grain niobium which underwent various oxidation processes. After initial buffered chemical polishing, anodization, baking in pure oxygen atmosphere and baking in air up to 180 °C was applied with the objective of clearly identifying the role of oxygen and the oxide layer on the Q-drop. During each rf test a temperature mapping system was used allowing to measure the local temperature rise of the cavity outer surface due to RF losses, which gives information about the losses location, their field dependence and space distribution on the RF surface. The results confirmed that the depth affected by baking is about 20 – 30 nm from the surface and showed that the Q-drop did not re-appear in a previously baked cavity by further baking at 120 °C in pure oxygen atmosphere or in air up to 180 °C. A statistic of the position of the “hot-spots” on the cavity surface showed that grain-boundaries are not the preferred location. An interesting correlation was found between the Q-drop onset, the quench field and the low-field energy gap, which supports the hypothesis of thermo-magnetic instability governing the Q-drop and the baking effect.

INTRODUCTION

Field emission free superconducting cavities made of high purity (RRR>200) bulk niobium show a severe degradation of the quality factor Q_0 as B_p exceeds ≈ 90 mT (Q-drop). An effective way of reducing the Q-drop is a low-temperature (100-140 °C) “in situ” baking (LTB) of the cavity in ultra-high vacuum (UHV) for several hours. A number of models have been proposed to explain the Q-drop and the baking effect but they all seem to contradict some of the experimental results, as described in recent reviews [1].

Measurements of low-field superconducting parameters such as the critical temperature (T_c), the penetration depth at 0 K (λ_0) and the normal-electrons mean free path (l) suggested that oxygen diffusion is involved in the effect of LTB on the cavity performance [2, 3]. Recently, a model based on reduced lower critical field due to higher interstitial oxygen near the surface has been refined to provide an explanation for the Q-drop and the baking effect [4]. In order to test the validity of this model we

tried to deliberately vary the oxygen content near the surface oxide layer by anodization, low-temperature baking in pure oxygen atmosphere, baking in air at higher temperatures and “in-situ” baking for shorter time. For this study we used a cavity made of large-grain niobium and we used a temperature mapping system to identify the location, field dependence and spatial distribution of the RF losses. Niobium samples have been treated together with the cavity and they have been analyzed with TEM and SIMS at North Carolina State University to further understand the modifications of the oxide layer and of the impurities (oxygen and hydrogen) distribution near the surface due to such treatments.

EXPERIMENTAL SETUP

The cavity used for this experimental study is a 1.5 GHz single cell with the same shape as the one used in the CEBAF accelerator. The ratios of peak surface electric and magnetic fields to the accelerating field are $E_p/E_{acc} = 1.78$, $B_p/E_{acc} = 4.43$ mT/(MV/m) as calculated with the SUPERFISH code. The cavity was built by standard deep drawing and electron beam welding fabrication methods, starting from two 3.175 mm thick Nb sheets, which were saw-cut from a large-grain ingot made by Ningxia, China. The residual resistivity ratio (RRR) of the sheets was approximately 330 and the Ta content was less than 150 wppm, as specified by the manufacturer.

The standard cavity preparation for rf testing consists of

- Ultrasonic degreasing for 20 min
- Buffered chemical polishing (BCP) with a mixture of HNO₃ (69%), HF (49%), H₃PO₄ (85%) 1:1:1 or 1:1:2 in volume at 25 °C removing about 20 μm of niobium from the inner cavity surface, in addition to initial removal of about 70 μm after the cavity fabrication.
- High pressure rinsing (HPR) with ultra-pure water at a pressure of 80 bar for 1 h
- Drying for 4 – 16 h in class 10 clean room
- Assembly of beam pipe flanges with input and output antenna and pump-out port using indium wire in a class 10 clean room
- The cavity is attached to a test stand and evacuated to about 10⁻⁷ mbar prior to cool-down to 1.7 K.

Before insertion in the vertical cryostat, a temperature mapping system consisting of an array of 576 100 Ω Allen-Bradley carbon resistors divided in 36 printed circuits boards spaced by 10°, is assembled on the cavity using Apiezon N grease as bonding agent. Details on the temperature mapping system can be found in [5]. The position of the thermometers on the cavity are identified by two numbers: the angular position from the reference

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mark on the cavity in degrees, 0 to 350, and the vertical position, 1 to 16, where 1 corresponds to the thermometer on the top beam tube near the cavity iris.

ANODIZATION

Anodization allows to electrochemically grow an amorphous Nb_2O_5 film whose thickness depends mainly on the voltage applied between the cavity (anode) and a cathode. For this study, the cavity is filled with NH_4OH (15%), and a constant voltage is applied between the cavity and a Nb rod inserted in the cavity. The current is limited to about 1 A ($\sim 1\text{mA}/\text{cm}^2$) and decays exponentially with time as the oxide thickens. The power supply is switched off when the current drops to about 100 mA. In these conditions we expect an oxide thickness corresponding to about 2 nm/V [6]. By anodizing successively at increasing voltages a cavity which was previously “in-situ” baked, we convert some of the niobium into oxide until eventually the Q-drop may re-occur. This could give some indications of the depth affected by the low-temperature baking.

Fig. 1 shows the results from a series of RF tests at 1.7 K after successive anodization of the surface of a baked cavity. The Q-drop re-occurs after anodizing at 40 V, consistently with earlier results obtained at Cornell [7]. A reduction of Δ/kT_c from ~ 1.92 to ~ 1.73 by anodizing at progressively higher voltages was inferred by fitting the temperature dependence of the low-field surface resistance $R_s(T)$ with the BCS theory.

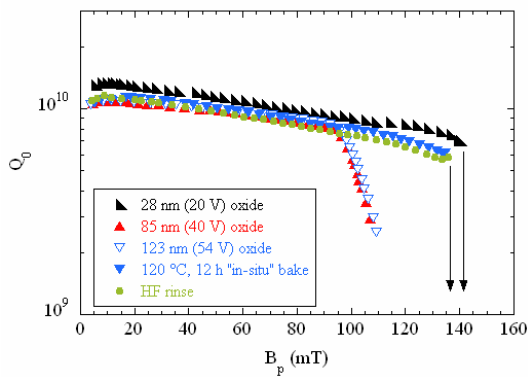


Figure 1: Q_0 vs. B_p measured at 1.7 K for several surface treatments indicated sequentially in the legend from top to bottom.

Fig. 2 shows T-maps at the highest field achieved after 40 V anodization and after UHV baking at 120 °C for 12 h, following the anodization experiments. Hot-spots are eliminated by baking. The growth of a new Nb_2O_5 layer following a rinse with HF did not restore the Q-drop, consistently with earlier results obtained at Saclay [8].

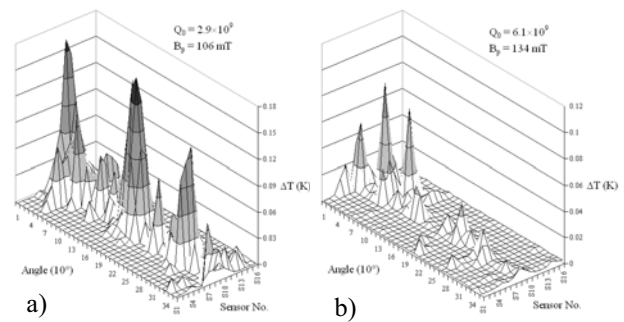


Figure 2: T-maps at the highest field achieved after 40 V anodization (a) and after 120 °C/12h UHV bake following anodizations (b), showing a strong reduction of hot-spots by baking.

BAKING IN PURE OXYGEN ATMOSPHERE AND IN AIR

Baking in Pure Oxygen Atmosphere

In order to further investigate the role of oxygen in causing the Q-drop we baked the cavity at 120 °C in 1 atm of pure oxygen as follows: the cavity was removed from the vertical test stand, placed inside the baking oven and connected to a vacuum line. Two fine-grain ($50 \times 50 \mu\text{m}^2$ average grain size) Nb samples were also inserted.

The cavity was evacuated to 6×10^{-9} mbar (water was the main residual gas), backfilled with research grade (99.9969% purity) oxygen up to 1 atm and baked for 12 h. Afterwards the Nb samples were stored in air while the cavity was high-pressure rinsed. There was no significant change of performance from the previous RF test (HF rinse) both at 1.7 K and 2.0 K: the residual resistance was unchanged, Δ/kT_c and quench field (which occurred at the same location) increased by about 2% and 5%, respectively. The temperature map at the breakdown field also did not show significant variations from the test before. The experiment was repeated and the duration of baking was increased to 48 h and the quench field and location did not change. The Q_0 vs. B_p plot at 1.7 K after baking for 48 h is shown in Fig. 3.

Baking in Air at Higher Temperature

The results from the oxygen baking tests suggested that the heating temperature may have not been high enough to diffuse oxygen through the oxide into the niobium. Therefore we decided to bake the cavity in air at higher temperatures: after disassembly and rinsing, the wet cavity was closed with two niobium discs clamped to the beam pipe openings and baked. Two fine-grain niobium samples were placed on the bottom disc inside the cavity. After baking, the cavity was degreased and high-pressure rinsed. This baking procedure was repeated for the baking temperatures of 120 °C, 150 °C and 180 °C for 12 h. The RF tests results, shown in Fig. 3 are summarized as follows:

- no significant variations of residual resistance, R_{res} , and quench field and location after baking at

120 °C. The T-map at the highest field (Fig. 4a) revealed some additional losses occurring also in the high electric field regions.

- Baking at 150 °C caused an increase of R_{res} by about 3 nΩ, and no change of quench field (~ 145 mT) or of its location (180-9). Nevertheless, there was some degradation of Q_0 at high field due to additional hot-spots, more or less uniformly distributed over the cavity area, including the irises
- Baking at 180 °C caused an increase of R_{res} by about 8 nΩ, a significant decrease of Δ/kT_c (~ 11%) and of the quench field (~ 18%) at the same location. The T-maps (Fig. 4b) showed a significant heating of the whole cavity surface. The Q_0 vs. B_p curve shows a quadratic-like degradation of Q_0 , not as sharp as for the Q-drop. The low-field BCS surface resistance at 4.3 K increased up to the same values as after chemical etching, due to the reduction of the gap parameter.

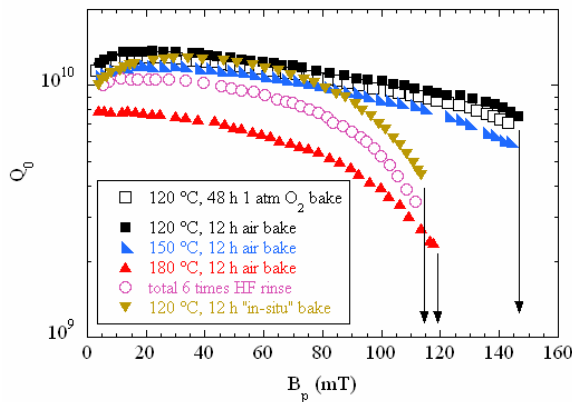


Figure 6: Q_0 vs. B_p measured at 1.7 K for several baking conditions. Baking at 180 °C in air caused a significant degradation of Q_0 and of the quench field which were not recovered by multiple HF rinses and by “in-situ” baking at 120 °C.

In order to determine whether the additional losses were due to the oxide layer, the cavity was rinsed with HF (49%) and re-oxidized in water for a total of six times. The test results showed a reduction of R_{res} down to the value prior to air baking (~ 20 nΩ) and of the intensity of some hot-spots. The quench location moved from 180-9 to 130-12. The Q_0 vs. B_p curve after the six HF rinses is shown in Fig. 3. Although the additional losses introduced by the air baking at higher temperature did not have the same field dependence as for the Q-drop, we applied the standard “in-situ” UHV baking procedure at 120 °C for 12 h to investigate whether they could also be reduced, but we did not succeed (The Q_0 vs. B_p curve is shown in Fig. 3). We tried to evaluate whether enough hydrogen from the wet surface could penetrate through the oxide layer to cause the so-called Q-disease during the baking at 180 °C. In order to do that, we hold the cavity in the cryostat at a temperature of 100 K for 40 h but the subsequent RF tests at 1.7 K and 2.0 K did not show any reduction of the low-

field Q_0 nor any variation of the Q_0 vs. B_p dependence from the previous test.

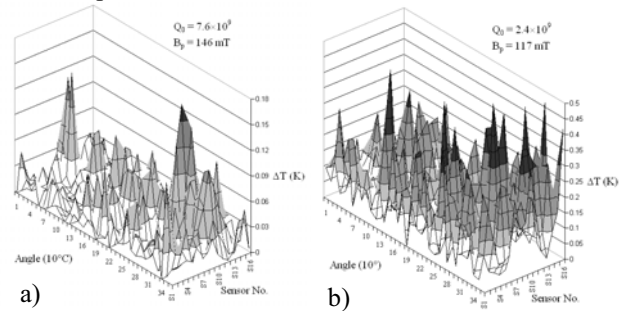


Figure 4: T-maps at the highest field achieved after 120°C/12h air baking (a) and after 180°C/12h air baking (b).

Niobium Samples Results

The results from the TEM measurements of the oxide thickness on the fine-grain polycrystalline Nb samples for different baking treatments showed no significant increase of the oxide thickness for the sample baked at 120 °C for 12 h in 1 atm of oxygen with respect to the reference sample (oxide thickness = 6.8 ± 0.1 nm), while the increase was 0.3 ± 0.1 nm for the second oxygen bake, for longer time (48 h). More significant increase, up to 3.3 ± 0.2 nm is observed after air baking at higher temperatures. The TEM pictures showed no identifiable suboxide regions. Fig. 5 shows the TEM micrograph for the sample baked in air at 180 °C for 12 h.

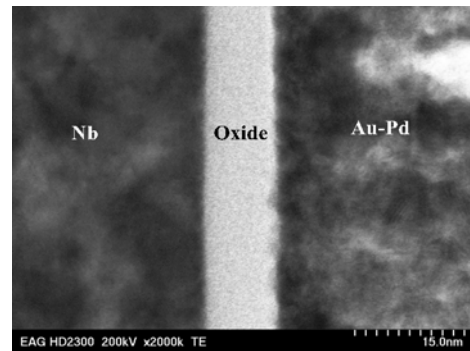


Figure 5: TEM cross-section micrograph of the sample baked in air at 180 °C for 12 h, showing a distinct oxide layer on the Nb surface.

The oxygen and hydrogen SIMS depth profiling relative to niobium for the reference sample (REF) and for the samples air baked for 12 h at 120 °C and 150 °C (W1), 120 °C only (W2) and 180 °C only (W3) are shown in Fig. 6. Carbon is present mainly at the surface. Higher oxygen counts over a larger depth than in the reference sample was found in all samples (including the ones baked in pure oxygen atmosphere). Depth resolution is degraded by the rough sample surface and by differential sputtering resulting from the differing sputter rates of the Nb crystallites of the polycrystalline Nb which are oriented at various angles to the SIMS primary ion beam. As a result, it is not possible to obtain oxygen diffusion

information from the O⁻ profiles. Hydrogen is depleted in the oxide layer and was at about the same high level inside the Nb for all samples. The width of the hydrogen depletion region is well correlated to the oxide thickness measured by TEM. An estimate of the hydrogen content based on a hydrogen implanted Si reference sample indicates concentrations of ~ 40 at. %. This value is very high and did not decrease significantly over a depth of about 15 μm. Details about the experimental technique can be found in [9]

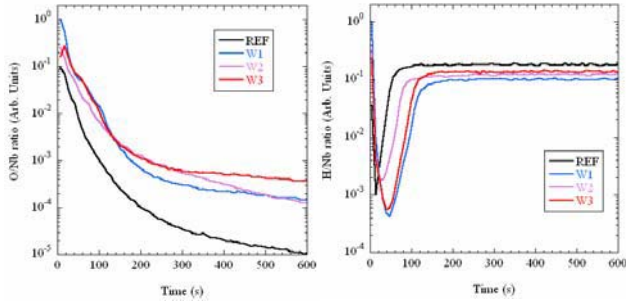


Figure 6: SIMS Oxygen (left) and Hydrogen (right) depth profiling for samples baked at different temperatures (Refer to text for a description of the labels).

HYDROGEN DEGASSING AND POSTPURIFICATION

In order to investigate the cause for the increase in the number of hot-spots introduced by the air baking at 180 °C and which were not significantly reduced by additional chemical etching, we wanted to evaluate the influence of interstitial impurities by heat treating the cavity in a vacuum furnace in two steps: at 600 °C first and at 1250 °C with titanium second. The heat treatments at 600 °C for 10 h or 800 °C for 3 h remove interstitial hydrogen from niobium and are commonly applied to niobium cavities to prevent Q-disease. For the second heat treatment, the cavity is placed in a titanium box and heated to 1250 °C. A titanium layer is evaporated on the cavity surface and acts as a getter for impurities such as oxygen, nitrogen and hydrogen.

After the first heat treatment at 600 °C, the cavity was etched by BCP 1:1:2, removing ~ 17 μm of material. The RF test was limited by Q-drop, with no field emission (Fig. 7). The residual resistance was only 3 nΩ. The T-maps still showed extended RF losses over the whole cavity surface and high thermal response from the thermometers (Fig. 8a). After UHV baking at 120 °C for 3 h no Q-drop was found up to a quench field of 125 mT. After the post-purification treatment, a ~ 55 μm thick layer was removed from the inner cavity surface by BCP 1:1:1. The baseline RF test showed Q-drop with no field emission (Fig. 7). The Q-drop onset was raised to 146 mT by “in-situ” baking at 120 °C for 3 h. An additional “in-situ” bake at 120 °C for 6 h eliminated the Q-drop up to the quench field (165 mT, at location 30-9). As it can be seen from the T-map after post-purification shown in Fig. 8b, it was only after this treatment that most of the cavity surface showed no distributed “anomalous” RF losses,

introduced after air baking at 180 °C, but only a few hot-spots in the equator region, similar to the map showed in Fig. 2a. Post-purification also restored the high quench field value which was obtained in the first tests.

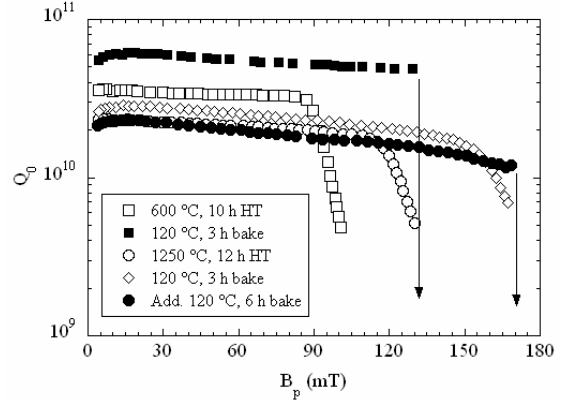


Figure 7: Q_0 vs. B_p measured at 1.7 K after hydrogen degassing at 600 °C and “in-situ” baking and after post-purification at 1250 °C and two consecutive “in-situ” baking.

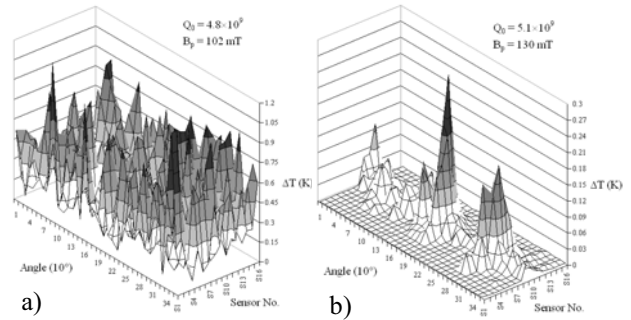


Figure 8: T-maps after hydrogen degassing at 600 °C (a) and after post-purification with Ti at 1250 °C (b).

ANALYSIS OF HIGH-FIELD DATA

The data show a good correlation between Δ/kT_c and the values of B_p corresponding to the onset of Q-drop and to a quench, for all the RF tests done on the single-cell cavity. This could be interpreted in a simple way, by considering the dependence of the breakdown magnetic field on the energy gap in the thermal feedback model and we obtain that a variation of the energy gap from a value Δ_0 to Δ changes the breakdown field from H_{p0} to H_p as follows [10]

$$H_p = H_{p0} e^{\frac{\Delta - \Delta_0}{2kT}} \quad (1)$$

A fit of the B_p -values corresponding to the onset of Q-drop and quench as a function of Δ with Eq. (1), shown in Fig. 9, give values of the fit parameters H_{p0} and Δ_0 consistent with the values of the critical field of Nb at 2 K and the gap value for pure Nb, respectively. Eq. (1) then suggests that the reduced gap-value obtained in a chemically polished niobium surface yields a reduced value of the critical field. The gap-value is raised by baking and so is the critical field.

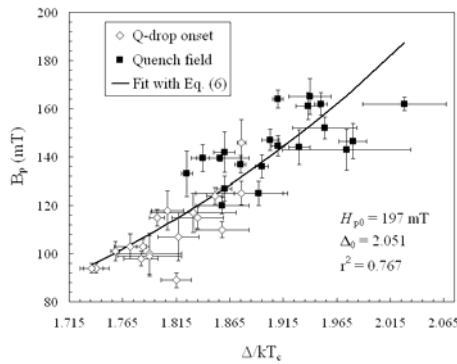


Figure 9: B_p -values at 2 K corresponding to the onset of Q-drop or quench as a function of Δ/kT_c fitted with Eq. (1) with H_{p0} and Δ_0 as fit parameters.

An analysis of the effect of hot-spots on the thermal balance of the cavity was presented in [11]. In the model, it is assumed that, besides the heat dissipated in the uniform part of the cavity, additional power is dissipated at a number of hot-spots with reduced superconducting properties. From a solution of the heat balance equation, a parametric dependence $Q_0(B_p)$ was obtained. This dependence provides a very good fit of the experimental Q_0 vs. B_p curves at 2.0 K and 1.7 K as shown in Fig. 10.

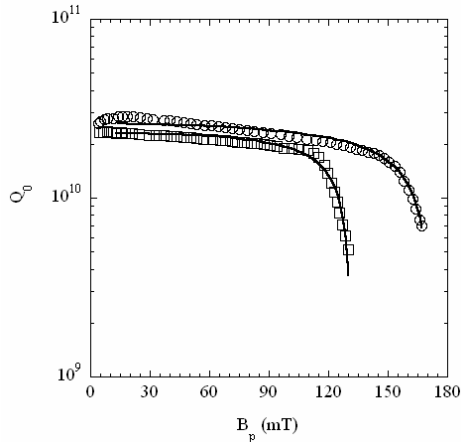


Figure 10: Q_0 vs. B_p data measured after post-purification (squares) and after 120 °C, 3h “in-situ” baking fitted with the model of Ref. [11] (solid lines).

CONCLUSIONS

The anodization and HF rinse tests reported in this article confirm previous results on small-grain polycrystalline cavities, for large-grain niobium cavities: “in-situ” baking affects the properties of niobium up to a depth of 20 – 30 nm and the growth of a new oxide layer on a baked cavity, after HF rinse, does not restore the Q-drop. The baked cavity was resistant against the occurrence of Q-drop even after oxygen injection by additional bake-outs in a pure oxygen atmosphere and in air, at higher temperatures. Sufficiently high oxygen concentrations, as achieved by baking in air at 180 °C for 12 h, introduced high RF losses, which were interpreted as due to higher dielectric and interface losses [10]. T-

maps showed that the only treatment which allowed a complete recovery from these losses was post-purification with Ti at 1250 °C. If the baking temperature is sufficiently low (≤ 120 °C), the oxide dissociation and oxygen injection from the surrounding atmosphere are minimal and a significant improvement of the Q-drop can be achieved by baking in air.

The onset of Q-drop in the large-grain cavity is raised above $B_p = 165$ mT after UHV bake at 120 °C for 9 h, which is shorter than the typical 48 h baking required on fine-grain cavities. This would help reducing the cavity preparation times, which is an important aspect for large-scale cavity production projects.

A correlation between the onset of Q-drop, the quench field and the energy gap emerges from the data, supporting the hypothesis of thermo-magnetic breakdown. The field dependence of the heat generated at hot-spots causing the Q-drop fit this description well. As for the physical origin of this phenomenon, the results presented are in contradiction with oxygen diffusion models. Hydrogen may be involved, although more systematic studies are necessary. The investigation of hydrogen in niobium by conventional surface analytical techniques is made difficult by its high mobility in Nb and by being present as the main residual gas in the analysis chambers. A well-trusted, reliable characterization method and procedure with high enough sensitivity is necessary for clear results. More detailed studies of the oxide/metal interface are also desirable to clearly identify the presence of suboxide clusters and modifications introduced by baking.

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