

MODIFICATION ON SURFACE OXIDE LAYER STRUCTURE AND SURFACE MORPHOLOGY OF NIOBIUM BY GCIB TREATMENTS*

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Abstract

Recently, it was demonstrated [1] that significant reductions in field emission on Nb surfaces could be achieved by means of a new surface treatment technique called gas cluster ion beam (GCIB). Further study revealed that GCIB treatments could also modify surface irregularities and remove surface asperities leading to a smoother surface finish as demonstrated through measurements using a 3-D profilometer, an atomic force microscope (AFM), and a scanning electron microscope (SEM). These experimental observations were supported by computer simulation via atomistic molecular dynamics and a phenomenological surface dynamics. Measurements employing a secondary ion mass spectrometry (SIMS) found that GCIB could also alter Nb surface oxide layer structure. Possible implications of the experimental results on the performance of Nb superconducting radio frequency cavities treated by GCIB will be discussed.

INTRODUCTION

Recent experiments [1-4] have shown that GCIB technique is a highly desirable tool for treating Nb surfaces to reducing field emission. In order to use this new technique in an optimized fashion, it is important to understand what kind of effects this new tool has on the treated Nb surfaces.

In this paper, we report on the results of a serials measurements on the surfaces of Nb samples treated by various GCIB gas species employing a 3-D profilometer, an AFM, an SEM, and a dynamic SIMS.

SAMPLES AND EXPERIMENTAL INSTRUMENTS

The samples used here were the same samples as those for the study reported in Ref. 2. The samples were fabricated from the same Nb batch. These were special samples designed particularly for doing field emission scan using the scanning field emission microscope built at JLab. After the fabrication, the samples were treated by the standard buffered chemical polishing (BCP) to remove a thickness of 150 μm from the surfaces. After the chemical treatments, the samples were first rinsed with DI

water followed by ultrasonic cleaning with micro for one hour and then rinsed again with DI water. Finally water on sample surfaces was blown away by dry nitrogen gun.

The study was done using the surface instruments built in the surface science lab at JLab. For a detailed description of the instruments, please consult Ref. 5.

MODIFICATION ON SURFACE MORPHOLOGY OF NB BY GCIB

One of the most important effects from GCIB treatments is the ability to modify the morphology of the surface under treatments. This effect is relevant to the performance of Nb SRF cavities, since smoother inner surface of a Nb SRF cavity tends to give better performance [6]. It is also an important factor contributing to the suppression of field emission as discussed above in Ref. 2. This section will deal with how GCIB treatments can modify the morphology of Nb surfaces. To study this effect, experimentally an atomic force microscope (AFM) and a high precision 3-D profilometer are employed and theoretically computer simulation via atomistic molecular dynamics and a phenomenological surface dynamics is used.

The ability of GCIB treatments for modifying Nb surfaces under the treatments manifests itself via the measurements of etching rates. The etching rates of Nb by NF_3+O_2 , Ar, and O_2 has been measured quantitatively [7]. NF_3+O_2 was found to have the highest etching rate of 5 $\text{nm}^2/\text{cm}^2/\text{S}$ at 35 kV acceleration voltage.

Typical examples of profilometer measurements on a NF_3+O_2 treated Nb sample are shown in Fig. 1 for the untreated and treated halves respectively. In general, NF_3+O_2 GCIB treatment using this particular set of treatment parameters does not make the surface smoother. Typically the RMS of the treated region is 615 nm over an area of 200X200 μm^2 as compared with 315 nm for the untreated region. It seems that there are some shallow craters generated by NF_3+O_2 GCIB treatment on the treated region. Part of the reason for creating the craters can be due to the larger mass involved in NF_3 clusters. Therefore mechanical impact on the treated surface is much larger than that when employing much lighter clusters such as, for instance, O_2 . More study is needed in order to optimize NF_3+O_2 GCIB treatments on Nb.

Profilometer measurements on an O_2 treated sample, on the other hand, did not see any clear differences between the treated and untreated regions as shown typically in

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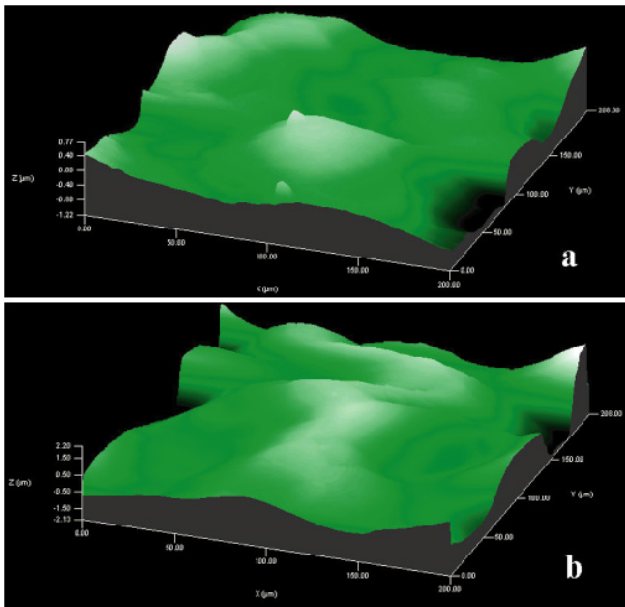


Figure 1: Typical profilometer images of $200 \times 208 \mu\text{m}^2$ of a) an untreated region and b) a treated region obtained on a BCP Nb coupon treated by $\text{NF}_3 + \text{O}_2$ GCIB.

Fig. 2. The RMS extracted from the scans varies from location to location and it oscillated around $1.27 \mu\text{m}$ depending on where the scans were done. The average RMS didn't correlate with a region regarding whether it was treated by O_2 GCIB.

However, we know that O_2 GCIB treatments do etch away materials from Nb surface [7]. Therefore we tried to do a more detailed study employing an AFM. In this case, a Nb coupon was divided into four quadrants as

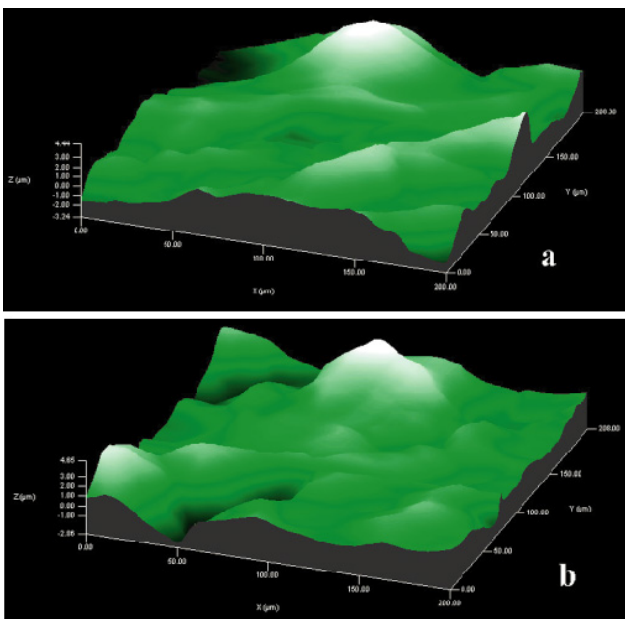


Figure 2: Typical profilometer images of $200 \times 208 \mu\text{m}^2$ of a) an untreated region and b) a treated region obtained on a BCP Nb coupon treated by O_2 GCIB.

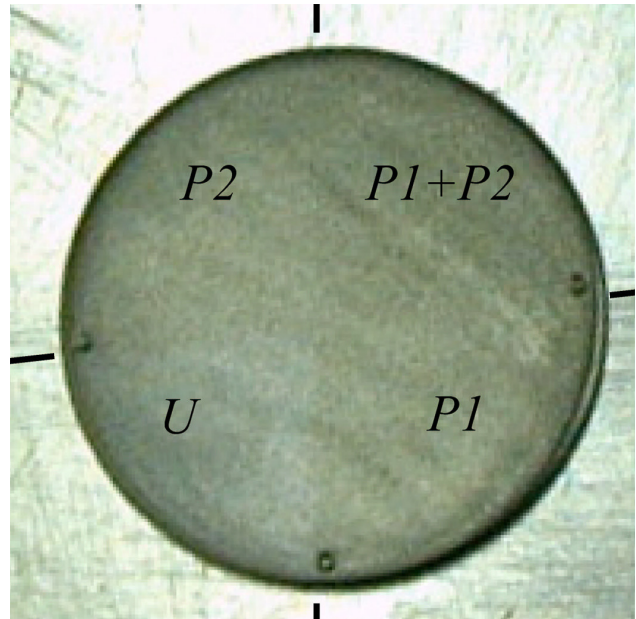


Figure 3: A Nb coupon was masked into equal quadrants for treatment with high and low energies O_2 GCIB (see the text for more details).

shown in Fig. 3. The region marked “U” means that it was untreated, “P1” means it was treated at 25 kV, “P2” means it was treated at 5 kV, and “P1+P2” means it was treated at 25 kV first followed by treatment at 5 kV. This was inspired by the fact that GCIB treatments with an initial etch rate followed by one or more lower etch rates can minimize the remaining roughness of the final surface and minimize material removal in order to attain a desirable level of smoothness [8]. AFM measurements were carried out using a Nanoscope IV controller

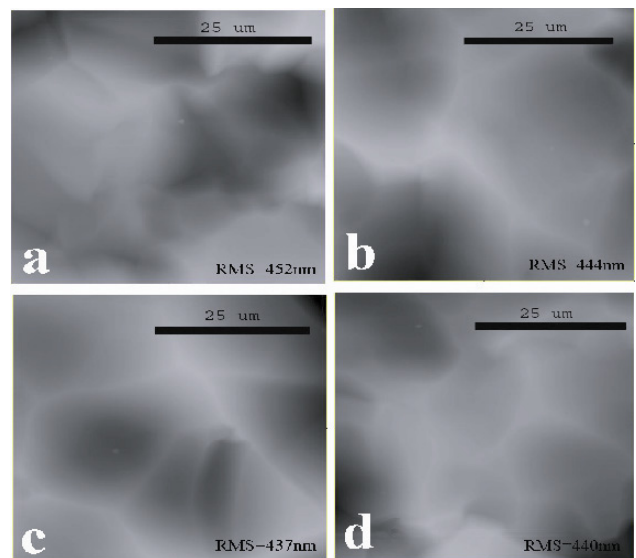


Figure 4: Typical AFM images of $50 \times 50 \mu\text{m}^2$ obtained on the sample shown in Fig. 3. a) for untreated region, b) for “P1” treated region, c) for “P1+P2” treated region, and d) for “P2” treated region.

dimension 310™ SPM head. Tapping mode was used in all the observations shown in this Section.

Figure 4 shows typical AFM images obtained on all the four quadrants of the sample with a scanning size of 50μmX50μm. The untreated region is rougher than the rest of the four quadrants. “P1+P2” treated region is indeed smoother than that treated by either “P1” or “P2”, which is consistent with the suggestions made in reference 25. It seems that the region treated at 5 kV is a little smoother than that treated at 25 kV.

COMPUTER SIMULATION

To understand the intrinsic mechanism associated with the modifications of morphology on Nb surfaces by GCIB treatments, computer simulations through molecular dynamic modeling were employed. Ar and O₂ were selected as the species for the GCIB clusters. Nb surface that would be treated by GCIB was supposed to be (1,0,0). Assuming that each cluster was multiply charged and contained 429 molecules or atoms, it was found that heavier GCIB species such as Ar could generate larger and deeper craters than those generated by lighter GCIB species on a Nb surface as shown in Fig. 5. In the simulation here, the kinetic energy of Ar was assumed to be 125 eV/atom and that of O₂ was 100 eV/molecule. This could explain the results found from the profilometer measurements on the samples treated by O₂ as shown in Figs.1 and 4.

Smoothing effect by GCIB treatments was demonstrated by modeling a Nb surface containing two types of surface tips with significantly different sizes.

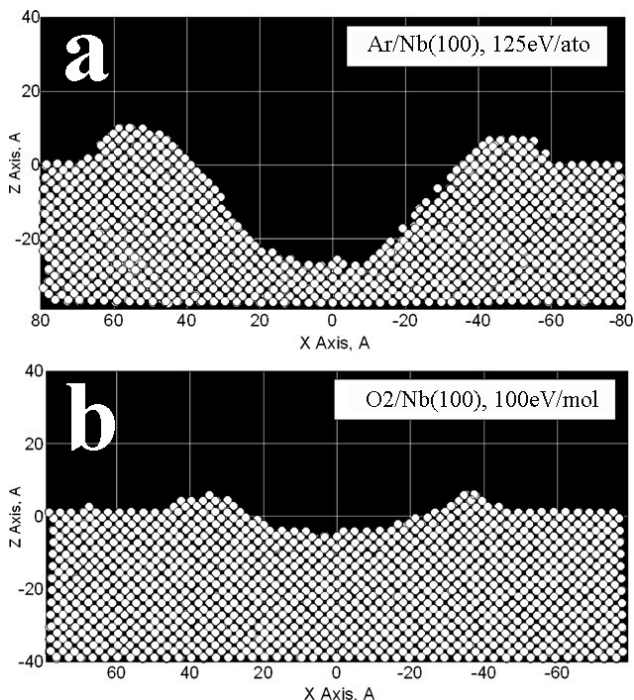


Figure 5: Craters formed on the surface of (100) Nb treated with a) clusters of 429 Ar at 125 eV/atom, and b) clusters of 429 O₂ at 100 eV/molecule, as calculated by computer simulation via molecular dynamics.

06 Material studies

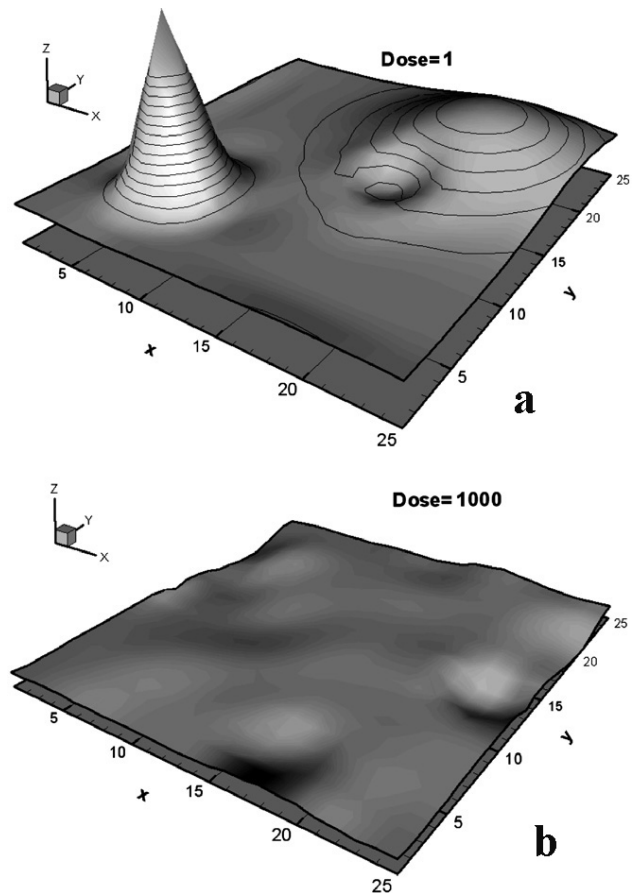


Figure 6: Results of mesoscale modeling of a Nb surface irradiated by O₂ cluster ion beam at a dose of 10¹³ ions/cm². The cluster energy was 30 KeV and the cluster size was about 3000 oxygen molecules in a cluster. The surface contained two types of features: narrow and tall and wide and short (represented in a)).

One tip was a narrow and tall hill with a typical diameter of a few nm. The other was a wide and short hill having a typical diameter of many tens of nm. Both tips had equal volumes and were schematically shown in Fig. 6a. The total modeled area was in the order of 10⁶–10⁷ Å², and this area was irradiated by up to 1000 30 keV O₂ clusters. The clusters randomly bombarded the whole area of the simulation cell. The cluster dose was in the order of 10³–10⁴ cluster/cell. The typical irradiation parameters used for surface smoothing were as follows: cluster ion doses were in the range of 10¹²–10¹⁵ ion/cm², average cluster sizes were in the order of 10³ atoms or molecules, and the total cluster energies was 30 keV. Displacements of surface particles after the cluster impact were modeled in accordance with the probability, obtained in our molecule dynamic simulation of a single cluster ion impact on a flat or inclined Nb surface.

Figure 6 demonstrates the results of our mesoscale simulations for Nb surface smoothing. The residual roughness is always defined by the geometry of an individual crater and increases with the increase of the total cluster ion energy. This explains why the region

treated at 25 kV in Fig.4 is a bit rougher than that treated at 5 kV. The simulation showed that the narrower hill could be removed by an irradiation dose that was five times lower than that required for the blunt hill. The larger the surface bump is in the horizontal plane, the higher irradiation dose is needed to completely remove the hill and smooth the surface. It is known that the narrower hills have a higher chemical potential than those with a larger diameter. Therefore chemically inactive GCIB surface treatments should remove the narrow hills faster than the wider ones. Computer simulation seems to suggest that the surface smoothing of Nb is mostly done by physical removal of the hills through mechanical interactions between the incoming GCIB clusters and the atoms of the treated surfaces rather than by chemical reaction. For details about this computer simulation study, please read reference 9.

MODIFICATIONS OF NB SURFACE OXIDE LAYER STRUCTURE BY GCIB

It is well known that the performance of Nb SRF cavities depends critically on their surface top layer of about 50 nm deep. The out most layer of any Nb surface is always covered with an oxide layer. We used to believe that the thickness of the oxide layer was approximately 6 nm. However, the latest atomically resolved TEM cross-section images [10] show that the oxide layer is much thinner for BCP and BEP [11] treated Nb samples. Most of the oxides in this top layer are Nb pent-oxides that are dielectric and are generally believed to have no negative effects on the performance of Nb SRF cavities. However, some Nb sub-oxides might exist [10] at the interface between the Nb₂O₅ and pure Nb such as, for instance, Nb₂O or NbO or others that may not be

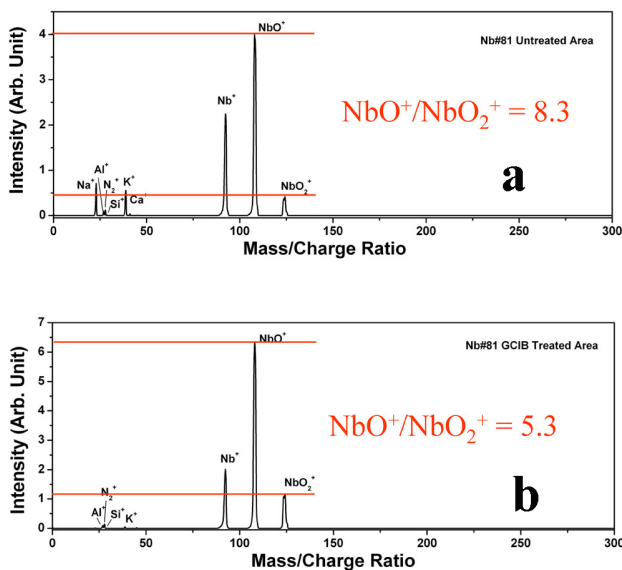


Figure 7: Typical SIMS whole spectrum measurements done on a) untreated region of a BCP Nb coupon treated by O₂ GCIB and b) treated region of a BCP Nb coupon treated by O₂ GCIB.

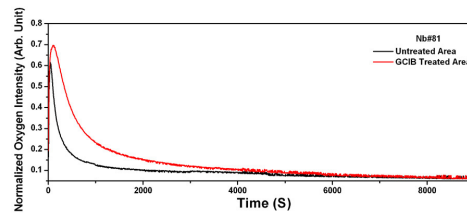


Fig. 8: Typical SIMS depth profile measurements done on a BCP Nb coupon treated by O₂ GCIB.

superconducting or may be superconducting at lower critical temperatures than that of Nb₂O₅. These sub-oxides can definitely cause RF losses and degrade the RF performance of Nb cavities. It is shown in this section that GCIB treatments can modify the surface oxide layer structure of Nb.

To study the modification of the surface oxide layer structure of Nb by GCIB treatments, a home-made dynamic SIMS system [5] was employed. Ar⁺ was used as the primary ion source. Measurements were done at a vertical incident angle, 2.5 keV, and 85 μA/cm². Both whole spectrum and depth profile were recorded. Depth profile measurements were done via a method described in Ref.12. Nb coupons were treated by NF₃+O₂, O₂, and N₂. Ar was not used since it might create confusions for the interpretation of the experimental results since the primary ion source was Ar⁺.

Figure 7 shows the whole spectra for a Nb coupon of which half was treated by GCIB O₂ and the other half was untreated. Depth profile measurements are shown in Fig.8. From Figs. 7 and 8, we can see the following: 1) The Nb surface is cleaner after the GCIB treatment. Elements such as Na and Ca disappear completely after the treatments, while the intensities of other peaks (apart from Nb and its oxides) reduce. 2) Significant amount of oxygen is introduced to the surface layer of Nb and the thickness of the oxide layer of the treated area is increased as compared with that of the untreated area. The increase in the thickness of the top oxide layer contributes significantly to the suppression of field emission as discussed in Ref.2. This is because after O₂ GCIB treatment the particulates are attached to a Nb surface that has a dielectric layer with a thickness more than double than that before the O₂ GCIB treatment, which makes the onset field much higher in order to sustain field emission. The mechanism regarding how O₂ GCIB treatments could increase the thickness of the oxide layer is not completely clear at the present moment, since implantation is expected to be minimal in GCIB treatments as discussed in the previous sections. However, somehow probably O₂ GCIB treatments can enhance oxygen diffusion into the interior of Nb. 3) The cracking patterns of Nb and its oxides change significantly after the treatment. For instance, from the two whole spectra we see that Nb/NbO/NbO₂ is 6/11/1 for the untreated area and 6/22/4 for the treated area. 4) The normalized maximum intensity of the oxygen content is 0.084 higher for the treated area. This is an increase of 13.7% than that of the

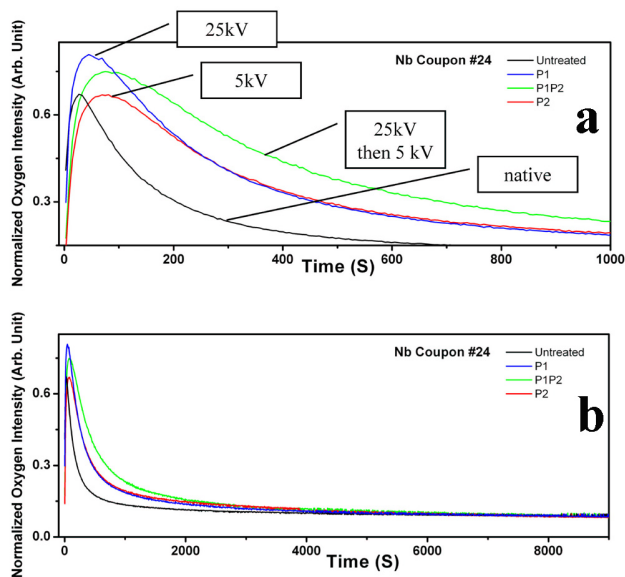


Figure 9: Typical SIMS depth profile measurements done on the BCP Nb coupon shown in Fig. 3. a) shows close-up plots of the depth profile data. b) shows the depth profiles measured on every quadrant.

untreated area. This implies that on the treated area, there can be an oxide layer with an oxidation state of $\text{Nb}_2\text{O}_{5+x}$ ($x > 0.5$). It is highly plausible that the extra oxygen atoms exist as interstitial atoms in the amorphous Nb_2O_5 layer. It seems that the treatment is not optimized, since the penetration of oxygen into the Nb surface is much too deep.

To explore the oxygen penetration effect, a Nb coupon was treated with different energies and durations in a way identical to that shown in Fig. 3. The treatment duration for “P1+P2” region was twice as much as that for “P1” or “P2” region. Oxygen depth profile data are plotted in Fig. 9. Fig. 9 tells us that the depth of oxygen penetration depends only on the duration of the GCIB treatment and has nothing to do with the treatment energy inside the energy window selected in this study. Higher treatment energy increases only the maximum intensity of the oxygen peak and its location, implying that probably more interstitial oxygen atoms exist in the Nb_2O_5 layer for the region treated at 25 kV. Therefore, GCIB treatment time has to be optimized in order to create a sharp interface between Nb_2O_5 and pure Nb. This work has not been done yet.

SIMS measurements were also done on NF_3+O_2 and N_2 treated Nb coupons. Due to the limited space here, readers are referred to Ref. 1 for the details. In all cases studied up to now, modifications of surface oxide layer structure were found.

SUMMARY

To summarize up, this paper reported on the investigation of the change of Nb surface morphology and oxide layer structure by GCIB treated via measurements by a 3-D profilometer, an AFM, an SEM, and a dynamic SIMS system. Theoretically computer simulation through atomistic molecular dynamics and a phenomenological surface dynamics was employed to help understand the experimental results. It was found that GCIB treatments could remove sharp features on Nb surfaces and could sometimes smash particulates into some smaller and smoother pieces that might not field emit. SIMS study showed that surface oxide layer structure could be tailored with GCIB treatments by using an appropriate treating agent such as, for instance, O_2 . Due to its effectiveness at changing the depth and composition of the surface oxide layer structure of Nb, GCIB might be a key to understanding and overcoming the limitations of the high-field Q-slope. More work is needed in order to fully explore this research topic.

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