

Impact of thermal annealing on stress, morphology, and field emission of NbTiN thin films

Frederic Braun[✉], Florian Brockner[✉], and Dirk Lützenkirchen-Hecht[✉]

University of Wuppertal, Gaußstraße 20, 42119 Wuppertal, Germany



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NbTiN thin films are promising candidates for superconducting multilayer structures aimed at surpassing the intrinsic field limits of bulk Nb in superconducting radio-frequency (SRF) cavities. In this work, Nb_{0.75}Ti_{0.25}N films grown by plasma-enhanced atomic layer deposition were systematically investigated with respect to their crystalline structure, surface morphology, and field emission behavior in their as-deposited state, as well as after annealing in vacuum at 900 °C and 1000 °C, respectively. X-ray diffraction reveals that annealing induces significant grain growth, a pronounced (111)-texture, and a strong reduction of residual stress, with the 1000 °C samples exhibiting the most uniform and relaxed microstructure. Optical profilometry shows a clear decrease in macroscopic roughness by approximately 20%–25% after annealing, while atomic force microscopy measurements confirm that the nanoscale roughness remains low and largely unaffected by the heat treatments. Field emission scanning microscopy demonstrates that annealing substantially increases the onset field for electron field emission from values below 60 MV/m in the as-deposited state to 180–220 MV/m for annealed films, correlating with improved crystallinity, reduced stress, and enhanced film-substrate adhesion. Complementary ultraviolet photoelectrospectroscopy measurements yield a work function of $\Phi_{\text{NbTiN}} = (4.32 \pm 0.07)$ eV, supporting the interpretation of the field emission scanning microscope data. The combined results show that high-temperature annealing, particularly at 1000 °C, significantly enhances the structural and functional performance of NbTiN films, underscoring their potential for application in superconducting multilayer coatings for next-generation SRF cavities.

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I. INTRODUCTION

Superconducting radio-frequency (SRF) resonators form the core of modern particle accelerators, enabling high accelerating gradients with exceptionally low power dissipation. To date, bulk niobium has been the material of choice for SRF cavities due to its relatively high critical temperature T_c of 9.2 K, chemical stability, and well-developed and well-established fabrication processes [1]. However, the performance of pure niobium cavities is now approaching its theoretical limit. The achievable accelerating gradient, typically around $E_{\text{acc}} \approx 50$ MV/m, is constrained by the superheating field H_{sh} and by microscopic surface imperfections that trigger quenches [1]. To surpass these intrinsic limitations, current research efforts focus on the development of alternative superconducting materials with higher critical parameters. Compounds such as Nb₃Sn and NbTiN exhibit significantly higher critical temperatures

and upper critical magnetic fields (H_{c2}), which promise enhanced thermal stability and reduced surface losses under high-field operation. Nb₃Sn, for example, has a critical temperature of about 18 K and exhibits notably lower Bardeen-Cooper-Schrieffer (BCS) surface resistance at moderate fields [2]. NbTiN, with a T_c of up to 17 K, combines high chemical robustness with favorable thin-film deposition properties on niobium substrates, making it an attractive candidate for layered SRF structures [3]. A particularly promising route to further improve SRF performance is the implementation of multilayer superconducting systems, as proposed by Gurevich [4–6]. In this concept, thin superconducting films with high critical fields (e.g., NbTiN) are alternated with nanometer-scale dielectric spacer layers on top of a niobium substrate. This multilayer architecture is expected to shield the underlying Nb from high magnetic fields and to delay vortex penetration, thereby significantly increasing the effective field limit of the cavity surface [4–6].

The aim of the present work is the characterization of annealed NbTiN thin films developed for application in SRF cavities. Structural and electron field emission properties of the thin films are investigated, with particular attention to the influence of microstructure and interfaces

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on field emission performance. To obtain detailed insight into the field emission surface morphology and onset-field distribution, field emission scanning microscopy was employed as a primary analytical technique. A comprehensive understanding of these parameters is essential to advance the realization of SRF cavities that exceed the fundamental limits of bulk niobium.

II. EXPERIMENTAL

A. Field emission scanning microscopy

Field emission measurements were performed using a field emission scanning microscope (FESM) located at the University of Wuppertal [7]. The system consists of an ultrahigh vacuum (UHV) analysis chamber with a base pressure of 5×10^{-10} mbar and a separate, high-vacuum preparation chamber, connected via an UHV transfer stage. Samples are mounted on an *XYZ*-translation stage with a lateral resolution of 1 μm , enabling precise control of the tip-sample distance and the lateral position of the electron field emission measurement. A long-working-distance optical microscope is integrated into the system to monitor the tip-sample alignment. During measurements, a tungsten test tip of 280 μm diameter is positioned a few micrometers above the sample surface, and a voltage U of up to 10 kV is applied. Once the local electric field $E = \frac{U}{d}$ exceeds a certain threshold, an emission current $I(E)$ is detected using a low-noise amperemeter (Keithley 6485 Picoammeter). The current-voltage characteristics are given by the Fowler–Nordheim equation:

$$I(E) = \frac{AS(\beta E)^2}{\Phi} \exp\left(-\frac{B\Phi^{\frac{3}{2}}}{\beta E}\right), \quad (1)$$

with β as the geometric field enhancement factor, S as the effective area of emittance, Φ as the work function, and A and B as the Fowler–Nordheim constants [8]. Field emission parameters such as the field enhancement factor and onset field E_{on} can be extracted from the results by transforming Eq. (1) into $\log(\frac{I}{E^2})$ vs $\frac{1}{E}$ and fitting the data linearly. Although several modern extensions of the Fowler–Nordheim theory exist, including the Schottky–Nordheim barrier correction [9,10] and the generalized formulations developed by Forbes [11], the classical FN equation is used in this work. The generalized theories require detailed knowledge of additional material and geometry-dependent parameters such as the barrier-shape correction functions $v(y)$ and $t(y)$, the local field distribution, and the field-dependent enhancement factor $\beta(E)$. The correction functions $v(y)$ and $t(y)$ are close to unity for $E < 1000$ MV/m for metals and can therefore be neglected in the present analysis. For the NbTiN thin films, these quantities cannot be determined reliably, because the emission originates from polycrystalline surfaces with

spatially varying work function, grain boundaries, local defects, and unknown microscopic emitter geometries. Those factors are taken into account by separating the FN plot into its *Up*- and *Down*-sweep and fitting both branches independently, which allows reversible and irreversible changes to be distinguished in the emitter state, such as adsorption and desorption processes or local barrier modifications. Under such nonorthodox conditions, the generalized FN formalism cannot be applied without introducing assumptions that would add uncertainty rather than reduce it. The classical FN equation therefore provides the most transparent and reproducible way to extract onset fields and to compare samples consistently.

In this work, the onset field E_{on} is defined as the applied electric field at which a current of 1 nA is measured. Since the analysis in this work focuses on relative differences between samples rather than on an absolute determination of β or tunneling parameters, the classical formulation is sufficient and appropriate for interpreting the experimental data. It should be emphasized that the field enhancement factors β extracted from the Fowler–Nordheim plots represent effective parameters rather than true geometric enhancement factors. In the present measurements, the microscopic emitter geometry, the exact emission area, and possible spatial variations of the work function are not known. Consequently, the fitted β values incorporate not only effects related to geometric field enhancement but also surface morphology, grain boundaries, local defects, and work function variations. The determined β values are therefore used exclusively for a qualitative comparison of the field emission behavior between samples and processing conditions. No quantitative information on the actual emitter geometry or absolute emission area is implied by these values.

It should be noted that the field emission measurements performed with the FESM are carried out under static (dc) electric field conditions. The extracted onset fields therefore represent the local electric field required to initiate electron emission from microscopic surface features under dc bias. In contrast, SRF cavities operate under oscillating rf electromagnetic fields, where both electric and magnetic field components are present and where emission processes may be influenced by additional effects such as rf heating or time-dependent field enhancement. Moreover, field emission testing under dc conditions imposes even harsher conditions for the investigated materials [12], and thus, the determined onset fields can be expected to be even larger under rf conditions. Consequently, the onset fields obtained in this study cannot be directly translated into equivalent rf surface fields in SRF cavities. Instead, the FESM measurements provide a comparative metric to evaluate the relative field emission behavior of different samples and surface conditions. Such measurements are widely used to identify potential emission sites and to assess how processing steps, such as thermal annealing,

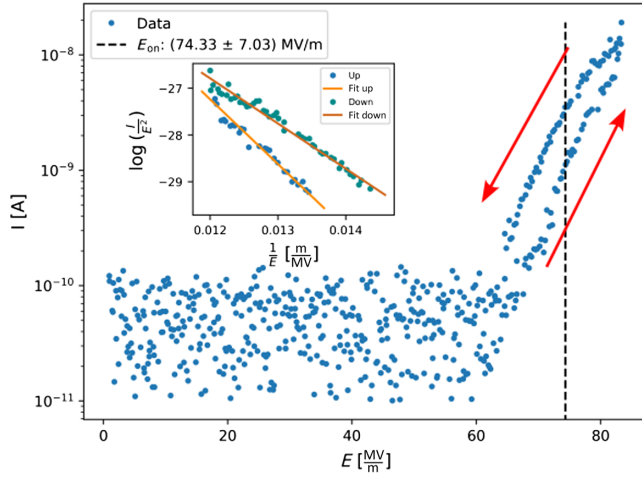


FIG. 1. Exemplary I-E curve of the NbTiN sample 1000C₁ annealed at 1000 °C with separately fitted *Up*- and *Down*-direction as provided in the inset.

influence the emission activity of superconducting thin films [13].

Figure 1 shows an exemplary current-field curve (I-E curve) from an annealed NbTiN sample with E_{on} marked at 1 nA and the transformed data. The I-E curve is separated into its *Up*- and *Down*-sweeps (increasing and decreasing voltage), and each branch is fitted independently to obtain the parameters β_1 and β_2 values for each direction as indicated in the inset of Fig. 1. The different slopes for the *Up*- and *Down*-sweeps suggest that the emission site undergoes irreversible changes during the voltage cycle, for example, through adsorption and desorption of light species or subtle modifications of the local emitter geometry.

All instruments, including the high-voltage supply, amperemeter, and motion controller, are operated via computer control. Custom measurement software and tip-fabrication procedures (see, e.g., Ref. [7]) were used to ensure reproducible emission conditions.

B. NbTiN sample system

The investigated samples consist of a multilayer structure comprising a silicon wafer substrate, an aluminium nitride (AlN) insulating layer, and a superconducting NbTiN top layer. The films were provided by González Díaz-Palacio, and details of the fabrication process can be found in Ref. [14]. All layers were deposited at 250 °C using plasma-enhanced atomic layer deposition (PE-ALD). For NbTiN, the chemical composition generally follows a $\text{Nb}_{1-x}\text{Ti}_x\text{N}$ composition, where the Nb/Ti ratio depends on the specific PE-ALD parameters. Previous electrical resistance measurements on the same NbTiN sample system have shown that $\text{Nb}_{0.75}\text{Ti}_{0.25}\text{N}$ films with a thickness of 60 nm exhibit maximum superconducting transition temperatures of up to approximately 15.9 K after thermal annealing, demonstrating the improvement of the

superconducting transport properties upon heat treatment [14]. Based on these results, the present work focuses on samples with a composition of $\text{Nb}_{0.75}\text{Ti}_{0.25}\text{N}$ and a NbTiN layer thickness of 60 and 15 nm insulating layer of AlN between the Si(100)-substrate and the NbTiN thin film. Three types of samples were investigated: as-deposited films; films annealed in high vacuum, $p = 10^{-6}$ mbar, for 60 min at 900 °C; and films annealed at 1000 °C, respectively. In the following, samples are labeled according to the scheme [annealing temperature]_[sample number]. In total, 10 samples were analyzed, consisting of 5 samples as-deposited, 3 samples treated at 900 °C, and 2 samples at 1000 °C. For clarity of presentation, most of the analysis is shown for one representative specimen (1000C₂), which exhibits the characteristic response of the investigated NbTiN films. The complete results for all 10 samples, including quantitative parameters and variations between specimens, are compiled in the tables provided in the respective sections.

III. RESULTS

A. X-ray diffraction measurements

The crystallographic properties of the NbTiN films were analyzed using x-ray diffraction (XRD). A simulated diffraction pattern of stress-free polycrystalline NbTiN, calculated from the structural parameters (space group: 225), which are given in Ref. [15], served as a reference. The reference pattern was generated using *PowderCell* [16] and provides the peak positions, lattice spacings, and intensity ratios expected for the reference material in comparison to the experimental data. XRD measurements were performed using a Malvern Panalytical (Almelo, Netherlands) X'Pert Pro diffractometer equipped with a Cu anode (40 kV/40 mA) in the Bragg-Brentano parafo-cussing geometry in a 2θ range of 32°–92° on an illuminated area of 10 mm × 10 mm, with acquisition times adjusted to ensure sufficient background counts and clear peak visibility. The analysis focuses on changes in crystal structure, macrostrain, and the crystallite sizes of the dominant orientations induced by annealing. Each measured peak is fitted using a double-Voigt function with an applied background implemented in a custom Python fitting routine. From the resulting fit parameters, the integral breadth is calculated and separated into its Gaussian and Cauchy components. The Gaussian component is associated with microstrain within the film, whereas the Cauchy component corresponds to the crystallite size [17], which was calculated via the Scherrer equation [18].

Figure 2(a) shows the XRD patterns of the as-deposited NbTiN samples, and Fig. 2(b) shows the annealed films in the relevant 2θ range. The full scan additionally contains the Si(400) peak at 69.14°, which is omitted here to improve the visibility of the NbTiN reflections. The two

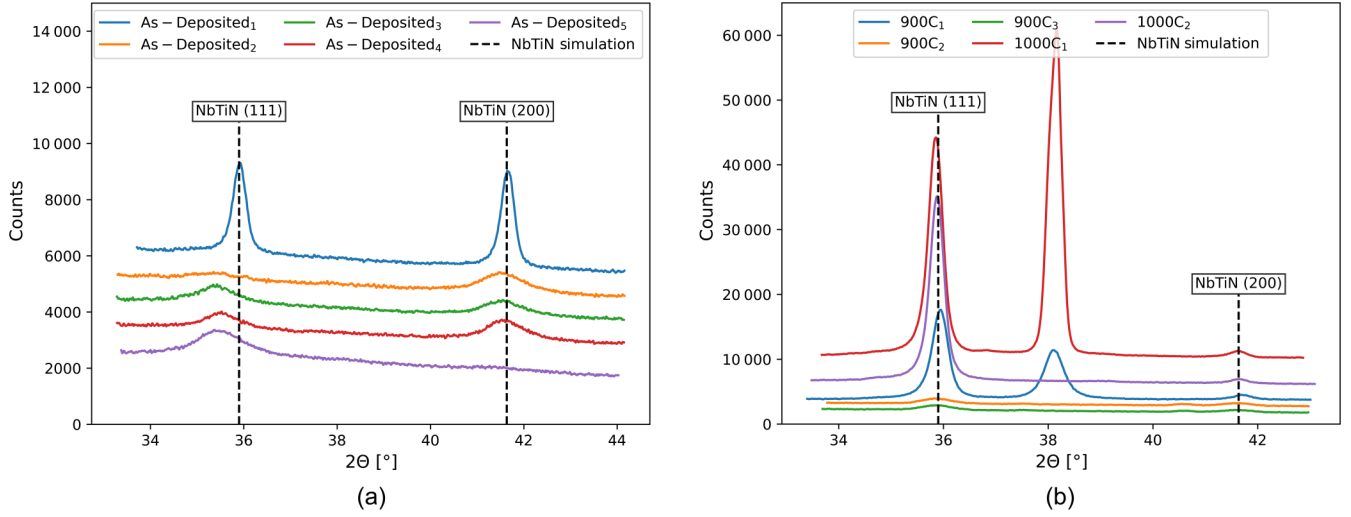


FIG. 2. (a) XRD data of the as-deposited and (b) annealed NbTiN samples in the relevant 2θ range. For better visibility, the diffractograms are vertically shifted. The unmarked peaks at $\approx 38^\circ$ originate from Nb(110) reflections of the sample holder.

unmarked peaks at approximately 38° correspond to Nb(110) reflections originating from the niobium sample holder and are therefore not considered in the analysis. Crystallite sizes L , residual stresses σ , and (111)/(200) peak ratios, obtained from peak fitting, are summarized in Table I. The macrostrain ϵ is calculated from the difference between the experimentally determined lattice spacing d_{exp} and the simulated stress-free value d_{sim} . Using the relation $\sigma = \epsilon Y_{\text{hkl}}$, the corresponding residual stress is obtained, where Y_{hkl} denotes the elastic modulus for the respective lattice plane. The orientation-dependent elastic moduli Y_{hkl} are calculated from the elastic stiffness tensors reported in ef. [19]. The as-deposited samples exhibit pronounced variations in peak intensity, width, and preferred orientation despite identical deposition conditions. *As-Deposited*₁ shows well-defined (111) and (200) peaks with crystallite sizes of several hundred Å, whereas

*As-Deposited*₂ to *As-Deposited*₅ display broad, low-intensity peaks, strongly varying (111)/(200) intensity ratios, and (111) peak shifts to substantially smaller Bragg angles, indicating increased lattice spacing. In several samples, one of the orientations is only weakly present or even absent. Weak peaks required estimation of crystallite size via full width at half maximum (FWHM) rather than Voigt deconvolution, as the single-Voigt approach becomes unreliable for thin films with low peak amplitudes. All as-deposited samples, except *As-Deposited*₁, exhibit larger lattice spacings than the stress-free simulation, suggesting significant tensile stress originating from the thermal expansion mismatch between NbTiN and Si. In contrast, the annealed samples show much more consistent diffraction behavior. All films exhibit a strong (111) preferred orientation, and peak shapes are significantly sharper. The 900 °C samples vary substantially in

TABLE I. Resulting crystallite size L , residual stress σ , and the (111)/(200) ratio obtained from the XRD data for all NbTiN samples.

Sample	(111)		(200)		(111)/(200) ratio
	L (Å)	σ (GPa)	L (Å)	σ (GPa)	
<i>As-Deposited</i> ₁	466.9 ± 0.2	-0.18 ± 0.01	427.2 ± 0.2	0.21 ± 0.03	0.92 ± 0.01
<i>As-Deposited</i> ₂	69.6 ± 16.3	3.06 ± 0.05	73.9 ± 0.2	1.79 ± 0.03	0.22 ± 0.04
<i>As-Deposited</i> ₃	68.8 ± 2.0	2.94 ± 0.02	77.5 ± 0.6	1.73 ± 0.03	1.35 ± 0.11
<i>As-Deposited</i> ₄	84.0 ± 0.3	2.24 ± 0.02	80.2 ± 0.4	1.09 ± 0.03	0.78 ± 0.05
<i>As-Deposited</i> ₅	63.0 ± 0.1	2.43 ± 0.01	[...]	[...]	[...]
900C ₁	582.6 ± 0.2	-0.32 ± 0.01	219.7 ± 0.2	-0.53 ± 0.03	14.85 ± 0.23
900C ₂	121.8 ± 0.8	0.06 ± 0.05	155.3 ± 4.3	0.76 ± 0.06	2.49 ± 0.19
900C ₃	120.7 ± 0.6	0.05 ± 0.02	145.8 ± 4.6	0.76 ± 0.03	1.84 ± 0.12
1000C ₁	598.7 ± 0.3	0.19 ± 0.02	435.6 ± 0.6	0.76 ± 0.03	31.04 ± 1.00
1000C ₂	457.0 ± 0.1	0.04 ± 0.01	316.7 ± 0.2	0.41 ± 0.03	38.34 ± 0.51

TABLE II. Compilation of macroscopic and microscopic surface roughness parameters R_a and R_z for the NbTiN samples obtained by OP and AFM.

Sample	OP		AFM	
	R_a (nm)	R_z (nm)	R_a (nm)	R_z (nm)
<i>As-Deposited</i> ₁	16.0 ± 0.5	111.0 ± 10.3	1.1 ± 0.1	5.9 ± 0.7
<i>As-Deposited</i> ₂	20.9 ± 0.6	147.0 ± 13.5	0.8 ± 0.2	5.6 ± 0.7
<i>As-Deposited</i> ₃	19.9 ± 0.7	139.3 ± 17.6	1.1 ± 0.1	6.4 ± 0.6
<i>As-Deposited</i> ₄	20.5 ± 0.7	144.6 ± 12.6	1.2 ± 0.1	7.1 ± 1.0
<i>As-Deposited</i> ₅	24.1 ± 1.2	173.4 ± 22.6	1.0 ± 0.1	7.2 ± 1.1
900C ₁	15.9 ± 0.6	114.1 ± 14.7	[...]	[...]
900C ₂	16.6 ± 1.6	111.9 ± 16.8	1.2 ± 0.5	8.3 ± 2.8
900C ₃	16.3 ± 0.5	113.4 ± 8.4	0.7 ± 0.1	4.2 ± 0.6
1000C ₁	14.2 ± 1.3	109.3 ± 44.8	[...]	[...]
1000C ₂	15.6 ± 0.5	110.1 ± 13.1	1.1 ± 0.2	5.7 ± 0.8

crystallite size, ranging from values similar to the as-deposited films to nearly the full film thickness of 60 nm, whereas both 1000 °C samples exhibit large crystallites indicative of extensive grain growth. The lattice spacings of the annealed films lie close to the simulated stress-free values, and the corresponding residual stresses are largely reduced, with the 1000 °C samples showing the lowest stress values, consistent with enhanced stress relaxation via grain coarsening and defect reduction.

This behavior matches the expected thermal evolution of stress in thin-film systems, where heating drives a transition from tensile to compressive stress followed by relaxation and a reduced tensile state upon cooling [20,21]. The (111)/(200) peak intensity ratio provides a clear fingerprint of the preferred orientation in the NbTiN films. For ideal, stoichiometric NbTiN, a ratio of 1.42 is expected, which was obtained by the simulated XRD pattern. The as-deposited samples show highly inconsistent orientation behavior, with ratios spanning from 0.22 to 1.35, demonstrating that nominally identical deposition conditions still produce films with strongly varying texture. This variability is consistent with the broad and weak diffraction peaks observed for the as-deposited sample set, where small differences in local growth conditions lead to pronounced fluctuations in crystallite size and stress.

In contrast, all annealed samples exhibit a strong and systematic enhancement of the (111) orientation. The ratios increase to values between 1.84 and 38.34, far exceeding the theoretical value of 1.42 and indicating a pronounced (111) texture that intensifies with annealing temperature. The extreme ratios observed for the 1000 °C films correlate with their large crystallite sizes, suggesting that high-temperature annealing not only promotes grain growth but also drives competitive texturing in favor of the (111) orientation. The combined trends in L , σ , and the (111)/(200) ratio show that annealing produces structurally homogeneous NbTiN films with strong (111) texture, reduced residual stress, and significantly enlarged crystallites, while the as-deposited

films exhibit the expected structural scatter of polycrystalline sputtered layers.

B. Surface roughness measurements

The optical profilometry (OP) measurements, using a Fries Research & Technology GmbH (Bergisch Gladbach, Germany) MicroProf, were conducted to investigate the morphology and surface structure of the films and reveal clear differences in the macroscopic roughness between the as-deposited and annealed NbTiN films. Exemplary OP measurements are shown in Fig. S1 in Supplemental Material [22]. The lateral resolution is 1 μm , and its vertical resolution is 3 nm. Three areas of 1 mm $\times$ 1 mm were measured per sample, and the results of the parameters were averaged. Independent of the processing condition, all OP maps show smooth and homogeneous surfaces without distinct morphological features or localized damage. Nevertheless, quantitative roughness analysis reveals pronounced differences between the sample sets, as summarized in Table II. The as-deposited samples exhibit the highest macroscopic roughness, with averaged roughness (R_a) values ranging from approximately 16 to 24 nm and peak-to-valley roughness (R_z) values between 111 and 173 nm. Within this group, *As-Deposited*₁ shows the lowest roughness, while *As-Deposited*₅ exhibits the highest, indicating substantial lateral growth inhomogeneities in the untreated state, as already deduced from the XRD measurements.

After annealing, the roughness decreases significantly. Both the 900 °C and 1000 °C samples exhibit consistently lower values, with $R_a \approx 14.0$ –16.6 nm and $R_z \approx 109.0$ –114.0 nm. Differences between the two annealing temperatures are minor, suggesting that increasing the annealing temperature from 900 °C to 1000 °C does not result in further substantial smoothing of the NbTiN surfaces. Overall, the results demonstrate that thermal annealing systematically reduces the macroscopic surface roughness,

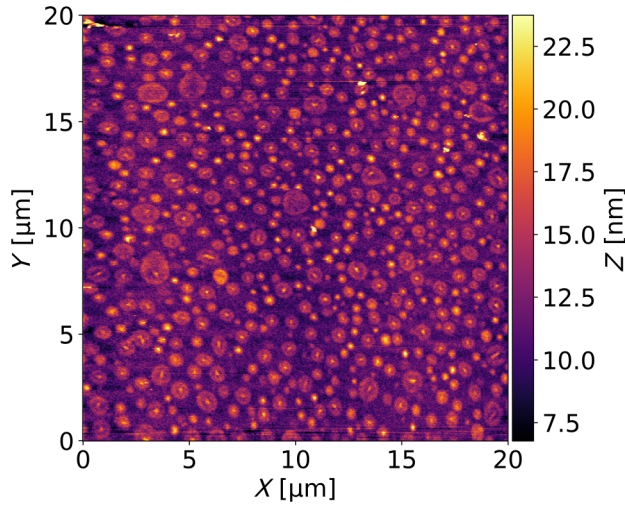


FIG. 3. Exemplary AFM measurement of sample *As-Deposited*₁ showing the nanoscale spots, which are also observed for 1000C₂.

consistent with thermally activated surface diffusion processes that promote a reduction in surface energy [23].

Atomic force microscopy (AFM) measurements were performed on $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ areas (500×500 pixels) in order to investigate microscopic surface structure, employing a Thorlabs EDU-AFM (Newton, New Jersey, USA), which resolves lateral features down to $\approx 10\text{ nm}$ and vertical variations of $1\text{--}5\text{ nm}$. Representative images of as-deposited and annealed films show generally smooth surfaces with only isolated small particles on some samples. Two samples, *As-Deposited*₁ and 1000C₂, exhibit numerous nanoscale spots across the surface. Figure 3 shows those spots exemplary for sample *As-Deposited*₁.

Additional AFM scans at multiple positions confirmed that these features are not local artifacts. Because these features were not observed in scanning electron microscopy (SEM) images and remained unchanged even after cleaning in ethanol and acetone solutions and dry air drying, they were identified by electron excited x-ray spectroscopy (EDX) depth profiling as carbon-rich contaminations located at the wafer surface beneath the NbTiN/AlN stack rather than on the film surface, as shown in Fig. S2 in Supplemental Material [22]. Roughness parameters R_a and R_z were extracted from the AFM topography, as seen in Table II. Samples affected by subsurface contamination show increased micro roughness, but masking the defective areas yields values comparable to the remaining films. For the as-deposited samples, the measured R_a values are consistent with those reported in Ref. [14]. Overall, the AFM results indicate that both as-deposited and annealed NbTiN films exhibit similar nanoscale roughness without a clear trend with annealing temperature, in contrast to the clear reduction in macroscopic roughness observed by optical profilometry. This apparent discrepancy between macroscopic and

nanoscale roughness is relevant for the interpretation of the field emission behavior in Sec. III C. Macroscopic roughness on the micrometer scale can lead to geometric field enhancement because larger topographic features locally increase the electric field at protrusions or edges. In contrast, the nanoscale roughness measured by AFM mainly reflects the intrinsic grain structure of the film and produces comparatively small variations in the local field enhancement. Consequently, a reduction in macroscopic roughness can significantly increase the emission onset field even if the nanoscale roughness remains largely unchanged. The AFM results therefore indicate that annealing primarily smooths the larger-scale surface morphology while leaving the nanoscale topography of the NbTiN grains essentially unaffected.

C. FESM measurements

FESM measurements were carried out for seven samples, including *As-Deposited*₁, *As-Deposited*₃, *As-Deposited*₅, 900C₁, 900C₂, 1000C₁, and 1000C₂. Those samples were chosen because their properties are representative for the full set. Because only a limited number of samples were available for each annealing condition, the comparison between 900°C and 1000°C treatments should be interpreted with appropriate caution. For each of those samples, varying areas between $1.2\text{ mm} \times 1.2\text{ mm}$ and $6.4\text{ mm} \times 6.4\text{ mm}$ were mapped by I-E-curves. For the first few measurements, the step size was set to $31.75\text{ }\mu\text{m}$ and the maximum allowed current was set to 50 nA . Later measurements show that a higher step size and a current limitation of 10 nA are better parameters to limit the possible destruction of the thin film. The adjusted step size of $317.50\text{ }\mu\text{m}$, in combination with the $250\text{ }\mu\text{m}$ test tip diameter, ensures that each measurement point is independent of the others. In contrast, the samples *As-Deposited*₃, 900C₁, and 1000C₁ were measured with a smaller step size, resulting in an overlap between adjacent measurement points, whereas all other samples were recorded without overlap.

According to Eq. (1), the work function is an important factor for field emission properties. Ultraviolet photoelectrospectroscopy (UPS) measurements were carried out for the samples *As-Deposited*₅, 900C₂, and 1000C₂ and yield an effective work function of $\Phi_{\text{NbTiN}} = (4.32 \pm 0.07)\text{ eV}$, which is lower compared to the work functions reported for TiN [24] and NbN [25]. The corresponding measurements are shown in Fig. S3 in Supplemental Material [22]. Proper *in situ* cleaning prior to the UPS measurements was not possible, which leads to surface contamination that likely affects the measured work functions. However, due to the fact that *in situ* cleaning like annealing or ion bombardment would change the surface morphology and therefore field emission properties of the samples, the resulting work function should provide an approximate value representative of the

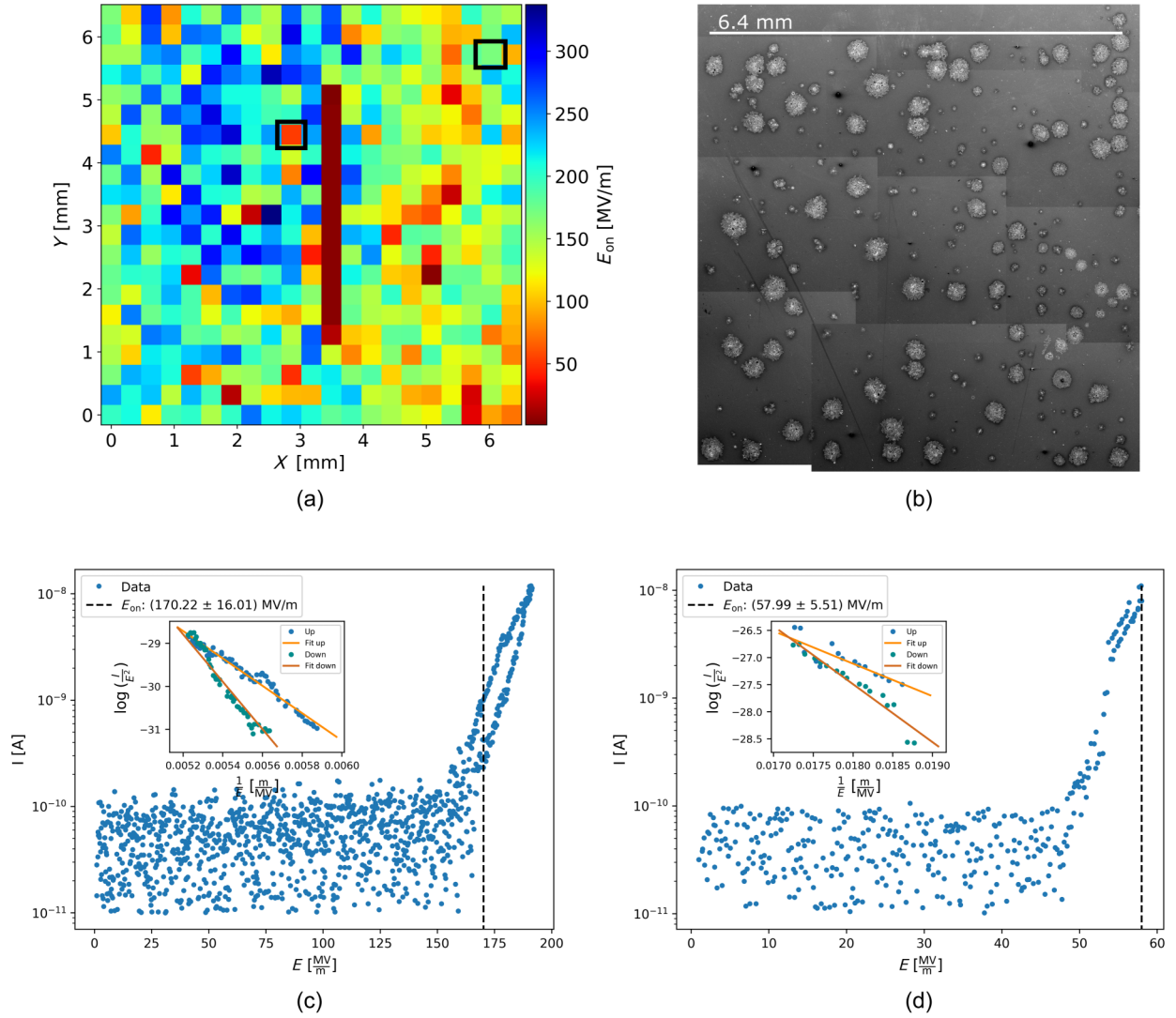


FIG. 4. (a) CCMMap and (b) related composite SEM image of the measured area from sample 1000C₂. Two exemplary I-E curves, (c) one with high E_{on} and (d) one with low E_{on} are marked in the CCMMap. Dashed vertical lines in (c), (d) represent the resulting onset fields. The insets depict the data in Fowler-Nordheim coordinates.

surface conditions during the FESM measurements. Independent work function measurements employing a Rikan AC2 photoelectron spectrometer in air also do not show work function variations between the different samples.

The onset fields obtained by the I-E curves can be mapped and plotted in a Constant-Current-Map (CCMap), which reveals the onset-field distribution of the surface as shown in Fig. 4(a). In the case of the sample 1000C₂, the step size was chosen such that there is no overlap with previously measured points. In addition to the CCMMap, an SEM image of the measured surface is shown in Fig. 4(b), assembled from multiple individual SEM images to cover the full measurement area.

The CCMMap reveals a nonuniform distribution of onset fields with values from < 25 to > 200 MV/m. In the upper-right region, significantly higher onset fields are

observed, whereas a narrow band of very low values appears near the center. This feature is most likely a measurement artifact and is removed by applying a threshold of $E_S = 25$ MV/m. Occasionally, isolated points with onset fields below 100 MV/m are recorded. Since each position is measured independently, these outliers are not correlated with neighboring points. Previous CCMMaps indicate that film damage can occur during both the *Up*- and *Down*-sweep of the voltage ramp. The locally reduced onset fields observed here suggest weakened film adhesion, potentially facilitating local delamination. A comparison with the SEM image [Fig. 4(b)] reveals circular damage features varying in size. Some features have roughly the same diameter as the tungsten test tip, but the majority of defects are substantially smaller. The two exemplary I-E curves in Fig. 4 illustrate the strong local variability of the electron emission properties. A region

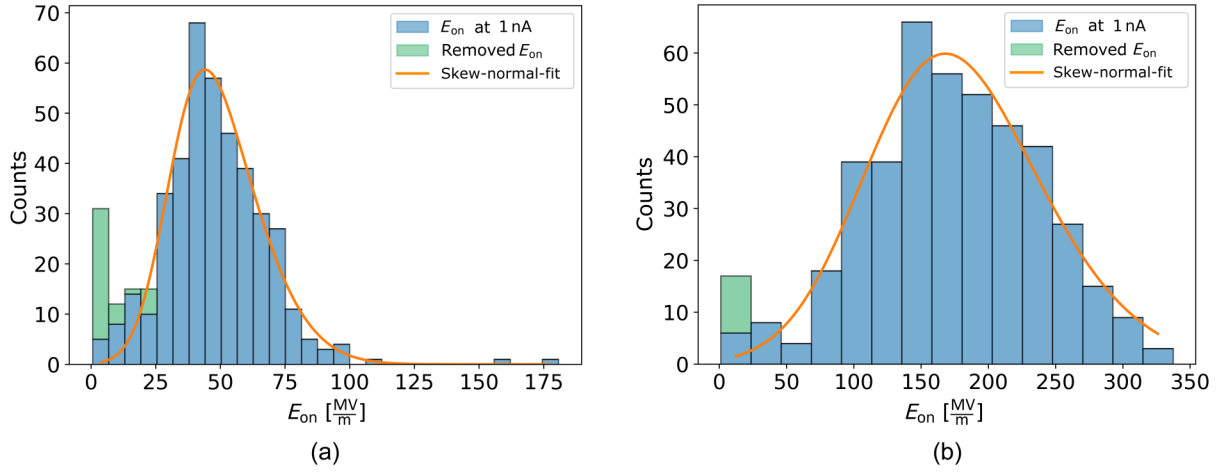


FIG. 5. (a) Histograms of samples *As-Deposited*₅ and (b) 1000C₂ obtained from the respective CCMaps.

with a low E_{on} shows a markedly steeper slope and earlier turn-on, while a region with a high E_{on} requires a substantially larger applied field. In both cases, the *Up*- and *Down*-sweep differ in slope, indicating changes in the local emitter morphology, such as adsorption and desorption or tip-shape modification occurring during the measurements. The corresponding onset fields are indicated in the figure by dashed vertical lines. By correlating the I-E curves with their respective measurement positions in the SEM images for all samples, it becomes evident that delamination can occur at any potential during the voltage sweep, in some cases even before measurable field emission sets in. These observations suggest that the film adhesion is locally reduced in some regions, allowing delamination to occur independently of field emission-induced heating. Additional I-E curves shown in Supplemental Material [22] further illustrate that individual emission sites can change their behavior during a single sweep, exhibiting discontinuities consistent with morphology changes occurring in real time (see Fig. S4 in Supplemental Material [22]). For further evaluation, a damage threshold was applied to each CCMMap to remove larger damaged structures or artifacts. After that, the remaining onset-field dataset was plotted in a histogram

and fitted with a skew-normal-distribution, yielding the mean onset field $\langle E_{\text{on}} \rangle$ as shown in Fig. 5.

For each sample, the damage threshold was selected individually such that only the damaged regions were filtered out. The comparison of the onset-field histograms of *As-Deposited*₅ and 1000C₂ shows that annealing leads to a pronounced increase in the mean onset field and a shift of the overall emission distribution toward higher fields. The mean onset fields obtained by all histograms of each sample are provided in Table III.

A comparison of the mean onset fields shows a significant increase after thermal treatment. In the as-deposited state, onset fields are typically in the range of 50–60 MV/m, whereas both annealing temperatures result in values between 180 and 230 MV/m. This behavior suggests that the as-deposited NbTiN layer is more susceptible to field-induced delamination under the applied electric fields. Nevertheless, the as-deposited samples, particularly sample *As-Deposited*₁, indicate that intact regions of the film can withstand fields of up to approximately 133 MV/m. Annealing at 1000 °C does not produce a clear improvement over annealing at 900 °C. Although sample 1000C₂ exhibits the lowest and sample 1000C₁ the highest mean onset field within the set of annealed samples, samples 900C₁ and 900C₂ show very similar values. Given the limited number of samples, no significant, statistically valid difference between the two annealing temperatures can be established. The present data therefore mainly indicate that thermal annealing in general improves the field emission performance of the NbTiN films, whereas possible differences between the two annealing temperatures remain suggestive and are partly masked by intersample variability. Part of the increase in onset fields can be attributed to a reduction in macroscopic surface roughness. The roughness values R_a and R_z of the annealed samples are about 30% lower than those of the as-deposited film (see Sec. III B and Table II), while the mean onset fields increase by a similar

TABLE III. Mean onset fields $\langle E_{\text{on}} \rangle$ for the NbTiN samples determined from the respective CCMaps.

Sample	$\langle E_{\text{on}} \rangle$ (MV/m)
<i>As-Deposited</i> ₁	133.9 ± 8.8
<i>As-Deposited</i> ₃	60.0 ± 10.0
<i>As-Deposited</i> ₅	49.2 ± 2.4
900C ₁	197.8 ± 3.4
900C ₂	185.2 ± 9.7
1000C ₁	235.1 ± 2.7
1000C ₂	178.5 ± 19.4

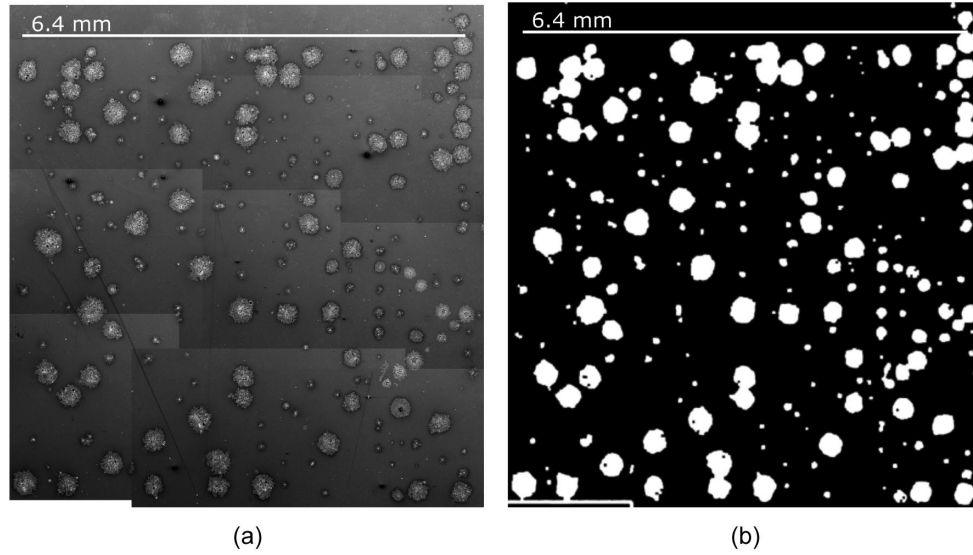


FIG. 6. (a) Composite SEM image and (b) resulting binary image of the measured area from sample 1000C₂. Damaged areas visible in (a) were identified by morphological transforms and are colored in white in (b).

factor. However, roughness alone cannot explain the observed improvement, as sample *As-Deposited*₁ exhibits its roughness and structural parameters comparable to the annealed films yet still shows significantly lower onset field values. A more plausible contribution is the reduction of defects or light element impurities (e.g., H, O, C) and contaminations during the annealing process. Such species may diffuse out of the film or segregate to grain boundaries, leading to a more homogeneous electronic structure and reduced local field enhancement. A comparable effect has been reported for Nb thin films and SRF cavities, where hydrogen removal during annealing increases the achievable field limit [26]. In addition to these effects, annealing appears to reduce the susceptibility of the NbTiN layer to field-induced delamination under the FESM measurement conditions also by reducing stress in the film volume (see Sec. III A and Table I), enabling the films to sustain higher electric fields before mechanical damage occurs. For more detailed evaluation, the SEM images of the measured areas were transformed into binary images where white pixels represent damaged and black

pixels undamaged areas. To ensure that the detected damage regions are represented accurately, morphological operators such as dilation and erosion are applied to the processed images using a custom Python implementation. Figure 6 shows the SEM image of sample 1000C₂ and its corresponding binary image.

From the binary image, the degree of damage η was calculated by dividing the number of damaged pixels by the total pixel count. By varying the parameter for dilation and erosion in the morphological operators for the image analysis, an error of 10% for each degree of damage is estimated. Table IV shows the calculated η for each sample.

A direct comparison reveals no clear correlation between the annealing temperature and the extent of surface damage. Sample *As-Deposited*₁ exhibits the lowest damage level despite the lack of heat treatment and the high contamination of the wafer. This is followed by the samples annealed at 1000 °C, although a noticeable difference in the damage parameter η is observed between samples 1000C₁ and 1000C₂. The remaining as-deposited samples and the 900 °C annealed samples show higher damage levels overall, with sample 900C₁ displaying the largest surface damage despite having undergone thermal treatment. To further contextualize these results, the damage levels are compared with the crystallite size L and the calculated residual stress σ , as shown in Fig. 7.

A comparison of the two plots indicates that high damage levels correlate with small crystallite sizes and elevated residual stress levels. The sample 900C₁ represents an exception. Although it exhibits large crystallites and low stress, it shows the highest damage level (see Fig. S5 in Supplemental Material [22]). This behavior is partly explained by the geometry of the field emission measurement for this sample. Due to the small step size,

TABLE IV. Calculated degree of damage η of all NbTiN samples obtained from its binary image.

Sample	$\eta \pm 10$ (%)
<i>As-Deposited</i> ₁	5.9
<i>As-Deposited</i> ₃	67.4
<i>As-Deposited</i> ₅	43.1
900C ₁	59.2
900C ₂	90.5
1000C ₁	28.3
1000C ₂	13.9

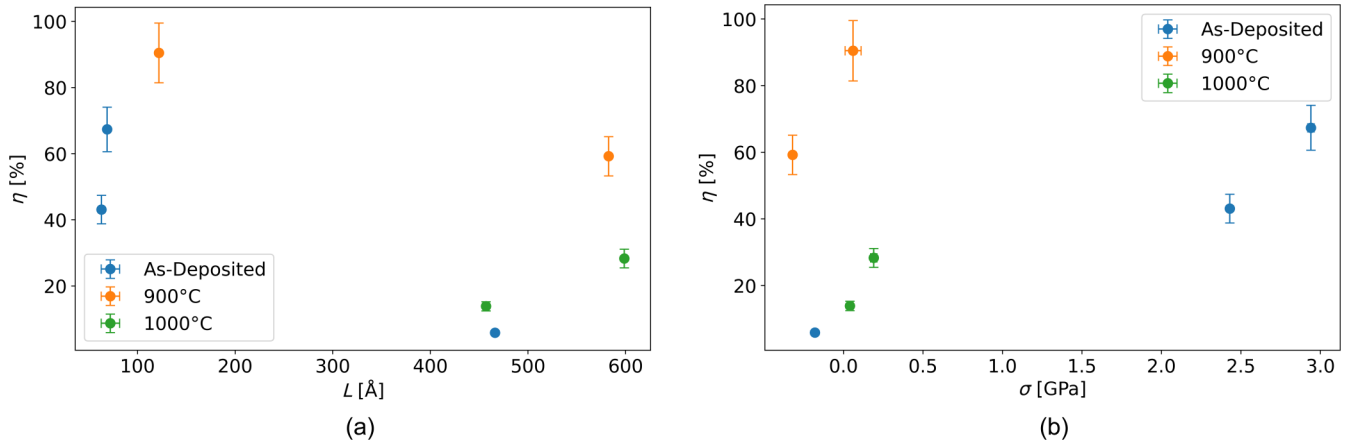


FIG. 7. (a) Relation of crystallite size L and (b) residual stress σ with the damage level η .

several measurement points overlapped with previously damaged regions, whose sharp edges and branched fracture patterns are highly susceptible to additional damage. A similar effect is observed for sample 1000C₁, where measurement overlap also occurred. However, the two samples annealed at 1000 °C exhibit comparatively low damage levels. Because of the limited number of samples and the observed intersample variability, this trend should be regarded as indicative rather than conclusive. The high damage level of sample 900C₂, despite the absence of overlap artifacts, supports the correlation between small crystallite sizes and increased susceptibility to field emission-induced damage. This is consistent with the role of grain boundaries as weak points that can act as initiation sites for degradation [27]. Larger residual stress further weakens grain boundaries and thus promotes damage formation. Interestingly, the samples *As-Deposited*₁ and 1000C₂ both grown on contaminated substrates exhibit the lowest damage levels. A possible explanation is that carbon-rich interlayers between substrate and film may act as compliant buffer layers that partially relieve thermal or intrinsic stresses, similar to effects reported for TiN/Ti multilayers [28] and AlN interlayers [29]. Consistent with this interpretation, these two samples also show the lowest residual stress values among all samples. In the case of sample 1000C₂, the combination of reduced stress and larger crystallites may compensate for the generally weaker interfacial stability and thus explain the comparatively low damage level observed under FESM conditions.

IV. CONCLUSION

In this work, annealed Nb_{0.75}Ti_{0.25}N thin films deposited by PE-ALD were investigated with respect to their structural, morphological, and field emission properties in view of their potential application in SRF cavity multilayer systems. The combined XRD, OP, AFM, UPS, and FESM analyses provide a consistent picture of how annealing

affects the microstructure and functional behavior of the films. XRD measurements reveal that annealing significantly improves the crystalline quality of NbTiN. While the as-deposited films exhibit large variations in preferred orientation, crystallite size, and residual stress, annealing leads to a pronounced grain growth, a dominant (111)-texture, and a substantial reduction of residual stress. Within the investigated sample set, the 1000 °C annealed samples tend to show the most uniform diffraction behavior, with crystallite sizes approaching the film thickness and lattice parameters close to stress-free reference values. Optical profilometry shows that annealing reduces the macroscopic surface roughness by approximately 20%–25%, independent of whether the films were annealed at 900 °C or 1000 °C. AFM measurements confirm that the nanoscale roughness remains low for all samples and does not systematically depend on annealing temperature. Through EDX depth profiling, localized features observed on some samples were identified as contamination at the substrate-film interface rather than surface defects. FESM measurements demonstrate that annealing strongly enhances the onset field of field emission. The as-deposited samples show low and highly inhomogeneous onset fields in the range of 50–80 MV/m due to weak film-substrate adhesion, whereas annealed samples reach significantly higher and more uniform onset fields of approximately 180–220 MV/m. The improvement correlates with the increased crystallite size and reduced residual stress after annealing and is consistent with a reduced susceptibility to field-induced delamination under the applied electric fields. UPS measurements yielded a work function of $\Phi_{\text{NbTiN}} = (4.32 \pm 0.07)$ eV, providing a reliable reference for interpreting the FESM data. Overall, the results demonstrate that postdeposition annealing is a highly effective route to improve the structural integrity, adhesion, and field emission resilience of NbTiN thin films. Within the investigated sample set, annealing at 1000 °C tends to produce a particularly homogeneous microstructure and high onset fields. However, given the limited number of

samples, this trend should be regarded as suggestive rather than statistically conclusive. These findings highlight the potential of annealed NbTiN as a promising candidate for superconducting multilayer structures intended to push SRF cavity performance beyond the intrinsic limits of bulk Nb.

V. SUPPLEMENTAL MATERIAL: IMPACT OF THERMAL ANNEALING ON STRESS, MORPHOLOGY, AND FIELD EMISSION OF NBTIN THIN FILMS

This section provides additional figures that support the main results of the manuscript *Impact of Thermal Annealing on Stress, Morphology, and Field Emission of NbTiN Thin Films*. Figure S1 in Supplemental Material [22] shows representative OP maps of an as-deposited and an annealed sample, illustrating the reduction in macroscopic surface roughness upon annealing. Figure S2 in Supplemental Material [22] presents the normalized EDX depth profile of sample *As-Deposited*₁, confirming that the detected carbon contamination is located at the wafer-film interface rather than on the NbTiN surface. Figure S3 in Supplemental Material [22] shows the UPS spectra used to determine the work function of the NbTiN films. Figure S4 in Supplemental Material [22] contains exemplary *I-V* curves demonstrating nonmonotonic changes during the voltage sweep, consistent with surface modifications occurring under high electric field. Figure S5 in Supplemental Material [22] shows the damaged NbTiN thin film of sample 900C₁ after FESM measurements with overlapping measurement positions.

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DATA AVAILABILITY

The data that support the findings of this article are openly available on [30]. A reference to this repository is made in the main text.

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