Nitridation of Nb surface by nanosecond and femtosecond laser pulses

Ashraf Hassan Farha^{1,4}, Osman Murat Ozkendir², Ulas Koroglu³, Yüksel Ufuktepe³ and Hani E. Elsayed-Ali^{1*}

¹*Department of Electrical and Computer Engineering and the Applied Research Center, Old Dominion University, Norfolk, Virginia 23529, USA*

²*Tarsus Technology Faculty, Mersin University, Tarsus 33480 TURKEY*

³*Department of Physics, Cukurova University, Adana, 01330, TURKEY*

⁴*Department of Physics, Faculty of Science, Ain Shams University, Cairo 11566, EGYPT*

**Corresponding author: (757)683-3749 (phone); (757)683-3220 (fax); helsayed@odu.edu*

Abstract

Niobium nitride samples were prepared by laser nitridation in a reactive nitrogen gas environment at room temperature using a Q-switched Nd:YAG nanosecond laser and a Ti:sapphire femtosecond laser. The effects of laser fluence on the formed phase, surface morphology, and electronic properties of the NbN_x were investigated. The samples were prepared at different nanosecond laser fluences up to 5.0±0.8 J/cm² at fixed nitrogen pressure of ~ 2.7×10⁴ Pa formed NbN_x with mainly the cubic δ-NbN phase. Femtosecond laser nitrided samples were prepared using laser fluences up to 1.3±0.3 mJ/cm² at ~ 4.0×10⁴ Pa nitrogen pressure. Laser induced ripple patterns oriented parallel to the beam polarization were formed with spacing that increases with the laser fluence. To achieve a laser-nitrided surface with desired crystal orientation the laser fluence is an important parameter that needs to be properly adjusted.

Keywords: Nitrides; Thin Films; Laser Annealing; Electron Microscopy; XANES.

1. Introduction

NbN_x thin films with phases that have good superconductivity and mechanical properties are motivating the study of methods to grow them and characterize their properties. These films are attractive in a wide range of applications, such as in microelectronics, optoelectronics, and for hard and corrosion protective coatings. Superconducting microelectronic applications of NbN_x films include the superconducting quantum interference devices (SQUIDs) [1], Radio frequency (RF) superconducting accelerator cavities [2], high-resolution X-ray detectors, superconducting quantum mixers [3], and superconducting single-photon detectors [4]. One of the techniques to obtain an NbN_x layer is by heating the Nb substrate at high temperature under a nitrogen gas environment [5]. Another method is laser nitriding by the irradiation of a metal surface in background nitrogen gas. Laser nitriding involves complex processes with a combination of many chemical and physical effects determining the properties of the nitrides [6]. The advantages of using pulsed laser heating to obtain nitrides over thermal nitriding include fast treatment, precise depth-profile control of the nitrogen content, adaptability to materials with different shapes, and applicability to materials that are sensitive to heat [7].

Conformal NbN_x coatings on Nb are important for RF cavities with very high quality factors. The new generation of accelerators employs superconducting Nb RF cavities to achieve the highest accelerating field. Hydrogen diffusion in Nb can adversely affect the performance of the superconducting RF (SRF) cavity. Nitriding the surface of Nb improves its mechanical properties by increasing hardness and wear resistance [2, 8-10]. A high-quality NbN_x coating can also provides a barrier layer for hydrogen diffusion into Nb for the potential application in SRF cavities.

Laser polishing is one of the methods used to smooth the surface of metals [8]. The scale of roughness is a critical factor in performances of SRF cavities [11]. We report on a study of nitriding parameters using ns and fs lasers at various laser fluences. The goal was to study the growth parameters to obtain different NbN_x phases and study the surface morphology of the grown NbN_x .

2. Experimental details

The Nb substrates were cut by wire electro-discharge machining from an Nb slice (CBMM Company, Brazil) to the dimensions of $8.6 \times 6.6 \times 0.7 \text{ mm}^3$. The surface preparation of the Nb was done in several steps. Before cutting the substrates, the surface of the Nb slice was mechanically polished with Al_2O_3 abrasive disks. The grain size of the Nb slice was several μm^2 , and, therefore, the samples were either single crystals or had a single grain boundary. Then, the buffered chemical polishing (BCP) method was used for etching the samples [12]. The BCP solutions (1:1:1 and 2:1:1 $\text{HPO}_3:\text{HNO}_3:\text{HF}$) were used at a temperature of 10°C during the cleaning process. Approximately a 50-micron layer of material was removed by BCP. The etched samples were rinsed in deionized water, and then dried under nitrogen flow. The surface roughness of the Nb substrate, measured by atomic force microscopy, gave a root-mean square (RMS) roughness of $0.6 - 1.0 \text{ nm}$ for $2 \times 2 \mu\text{m}^2$ scan area. After uploading the Nb substrate into the vacuum chamber, the chamber was pumped down to a vacuum of $\sim 8 \times 10^{-6} \text{ Pa}$.

The laser heating of the Nb substrates was done under nitrogen atmosphere. All samples were processed at room temperature. Two separate sets of experiments were performed at different laser fluences and nitrogen pressures. The laser fluence was measured just before entering into the chamber and corrected for losses in the glass viewport on the chamber. A Q-

switched Nd:YAG laser operating at 1064 nm wavelength with a pulse width of 40 ns and repetition rate of 10 Hz was used. The laser beam size on the Nb surface was $350\pm50\text{ }\mu\text{m}$, as measured by the knife-edge method at target equivalent plane. During nitridation, the sample was moved in the x-direction with a speed of $0.43\pm0.02\text{ mm/s}$, allowing the laser beam to raster the sample surface in the x-direction from one end to another, followed by a step of 0.05 mm in the y-direction until all the surface of the sample was scanned by the laser. The samples were exposed to different laser fluences up to $5.0\pm0.8\text{ J/cm}^2$ at room temperature and the same nitrogen pressure of $\sim 2.7\times 10^4\text{ Pa}$. The selection of this fixed pressure value of the nitrogen gas was done after performing laser nitridation at different nitrogen pressures in the range of $1.3\times 10^4 - 6.6\times 10^4\text{ Pa}$. Another laser used for nitridation was a femtosecond Ti:sapphire laser operating at a wavelength of 800 nm, pulse width of 100 fs, repetition rate of 1.0 kHz and beam size of $600\pm50\text{ }\mu\text{m}$. All samples processed by the fs laser were done at room temperature under constant nitrogen pressure of $4.0\times 10^4\text{ Pa}$. The laser fluence was up to $1.3\pm0.3\text{ mJ/cm}^2$. A similar sample-scanning method was used for processing with the ns Nd:YAG laser. The fluence used for ns- and fs-lasers is not similar since the threshold fluence for nitride formation is dependent on the laser pulse width. We compare the effect of ns and ns laser nitridation of Nb on nitride phase formation and surface texture.

Bruker-AXS three-circle diffractometer with graphite-monochromatic CuK_α radiation and a SMART Apex II CCD detector were used for the X-ray diffraction (XRD) measurements. XRD of the cleaned Nb substrate indicates that the Nb substrate exhibits crystallographic Nb with (110), (200), (211), and (310) orientations, as shown in Figure 1. The morphology of the samples was studied using a JEOL JSM-6060 LV scanning electron microscope (SEM). The SEM images were taken at an accelerating voltage of 20 kV. The chemical composition ($\text{N/Nb} =$

x) of the NbN_x samples was determined by electron probe micro analyzer (EPMA) point scan using a Cameca SX100.

X-ray absorption near edge structure (XANES) measurements were performed on beamline 8.2 at the Stanford Synchrotron Radiation Lightsource (SSRL) in SLAC National Accelerator Laboratory. The base pressure during the experiment was $\sim 2.0 \times 10^{-7}$ Pa. The total electron yield (TEY) mode was used by measuring the sample current. The current measurements were done using a low noise preamplifier Stanford Research System Model SR570. The incoming synchrotron beam flux (I_0) signal from a gold grid was used to normalize the spectra.

An FEI Quanta 3D FEG focused ion beam system was used to check thickness of the laser treated samples. An area of $30 \times 30 \mu\text{m}^2$ was coated with Pt to protect the surface of the sample as the ion beam was cutting into it. An accelerating voltage of 20 kV and working distance of 10 mm were used.

3. Results and discussion

3.1. X-ray absorption near edge structure (XANES) spectroscopy

XANES spectroscopy is one of the most powerful tools available for electronic structure determination. In XANES the X-ray energy is scanned and the effect of the absorbed X-ray is measured. Figure 1(a) shows normalized X-ray absorption spectra of NbN_x samples prepared at different ns laser fluences. The Nb- M_3 and M_2 edge spectra was recorded at room temperature in total electron yield (TEY) mode by measuring the drain current of the sample as a function of the photon energy. All TEY signals are normalized to I_0 , avoiding synchrotron dependent intensity variations. In addition, we have normalized TEY spectra of NbN_x films by subtracting a straight

line fitted to the region before the M_3 edge (below 365 eV) and adjusting the intensity of the spectra to 1 at 395 eV. The $M_{2,3}$ edge is mainly attributed to the transition of electrons from the Nb $3p$ state to unoccupied $4d$ and $5s$ states. The shape of Nb $M_{2,3}$ edges is similar for all the samples in Figure 1 (a), with two Nb $3p$ peaks split by about 15 eV due to the spin-orbit coupling of $4d$ electrons. The peaks at 365.5 and 380.8 eV are assigned to $3p_{3/2}$ and $3p_{1/2}$, respectively. Due to degeneracy, the peak at 365.5 eV always has a higher intensity than that at 380.8 eV [13].

Figure 1(b) shows measured $M_{2,3}$ intensity ratios as a function of ns laser fluence; we consider the integrated area under each M_3 and M_2 peak in Figure 1(a). The branching ratio (BR); $I(M_3) / I(M_2 + M_3)$ represents a high-spin-state, which is sensitive to the spin-states of $4d$ electrons. The absorption area of the M_3 and M_2 lines is the correct measure of their intensity, which is proportional to the oscillator strength of the $3p$ – $4d$ spin–orbit interaction and the local density of unoccupied final states in the system (i.e. the population of $4d$ holes). Therefore, the $M_{2,3}$ edge will be sensitive to transitions involving $4d$ holes [14]. Therefore, the BR should, hence, give information on the valence band spin-orbit interaction and the electrostatic interaction in the final state [13]. There must be a correlation between $4d$ occupancy and the BR in Figure 1(b). In the absence of electrostatic interaction and spin orbit coupling between core hole and d electrons the statistical ratio of BR is to be $2/3$. However, it varies depending on spin-orbit and electrostatic interactions [13, 15].

Figure 1(c) shows O K edge XANES spectra of samples processed at different laser fluences. The spectra were normalized by subtracting a straight line fitted to the region before the peaks (below 530 eV) and adjusting the intensity of the spectra to 1 at 555 eV. The O K edge is attributed to a transition of O $1s$ electrons to the unoccupied $2p$ states. The O K edge is characterized by a double-peak structure (peaks labeled a and b in Figure 1(c)) [16, 17]. The

relative height and energy splitting between these two peaks depend on the type of oxidation in the sample. The measured splitting between peaks *a* and *b* is about 4.4 eV, which is very close to that reported for the Nb₂O₅ oxidation state. This splitting was measured to be ~ 2.8 eV for NbO [18, 19], which is far from our measured value. Figure 1(c) shows that the shape of the K edge spectra is not similar, especially for peak *c*. In fact, the integrated intensity of peak *c* is strongest in Nb₂O₅ and decreases for lower valences [19]. We find a small change in the peak *c* intensity by calculating the integrated area under the peak. This intensity fluctuation may arise due to the effect of different NbN_xO_y structures. Oxinitride structures can be observed together with Nb₂O₅ structure in the NbN_x films grown on Nb [20].

The M_{2,3} edges for samples prepared by fs laser are shown in Figure 2(a). Nb M_{2,3} peaks at 365.5 and 380.8 eV have shoulders at ~ 368 and ~ 383 eV, respectively. This shape indicates presence of double peaks at these positions. These kind of double-peaks were reported for Nb-M₃ and Nb-M₂ lines when Nb₂O₅ is formed in the samples, but could not be detected for other oxide states [16, 18]. Also, no shifts are observed in both Nb 3*p* and N 1*s* peaks as the laser fluence is increased. If a niobium oxidation state other than Nb₂O₅ is found in the samples, there will be shifts by 1.4 eV or more in the position of the peak at 365.5 eV [16]. This confirms observations on O K edge that the Nb₂O₅ phase is formed in the samples. The source of this oxide layer could be a native layer on the Nb substrate, since niobium is highly reactive to oxygen, or on the surface of NbN_x samples that forms when handling samples in air.

Figure 2(b) shows measured M_{2,3} intensity ratios as a function of laser fluence. The BR shows small variations for fluences higher than 0.3 mJ/cm², which is due to the double peaks of Nb-M₃ and Nb-M₂ lines and different oxinitride structures. Therefore, the shoulders of the Nb 3*p*_{1/2} and 3*p*_{3/2} peaks are different for fluences higher than 0.3 mJ/cm² (Figure 2(a)). These

double-peaks for Nb-M₃ and Nb-M₂ lines were reported if Nb₂O₅ formed in the samples [16, 18]. Also, no shifts in both Nb 3*p* (M_{2,3}) and N 1*s* peaks (not shown here) were observed with the increase in the laser fluence. The O K edge XANES spectra of NbN samples prepared by using the fs laser is shown in Figure 2(c). The O K edge is characterized by a double-peak structure (*e* and *f* in Figure 2(c)) [16, 17]. The peaks labeled *e*, *f*, *g* and *h* are located at energies of 532.3, 536.6, 544.4 and 564.0 eV, respectively. The relative height and energy splitting between these peaks depend on the type of oxidation in the sample. The splitting between peaks *e* and *f* is about 4.2 eV, which is close to that reported for Nb₂O₅ [16].

The average BR intensity gives useful information on the 4*d* electron state related to chemical bonding and characteristics of the atom. Branching ratio shows only small variations for all samples, which suggests that 4*d* occupation is similar for most of the samples. Comparing the average BR of ns laser with fs laser samples (Figure 1(b) and Figure 2(b)), it appears that the average BR of ns laser samples (0.691) is higher than fs laser samples (0.680) which implies that spin-orbit coupling changed from the higher nitrogen ratio. This observation suggests that the higher nitrogen ratio in the sample (see Figures 4(b) and 6(b)) leads to the increase in vacancy of 4*d* states of Nb: that is Nb donates some amount of electrons to N and rising number of 4*d* holes in the NbN_x system. It has been previously shown that the BR intensity gradually increases with *d* electron population [13].

3.2. Structure and phase formation

Figure 3 shows the XRD patterns for samples prepared at different laser fluences from 1.8±0.3 to 5.0±0.8 J/cm² at the same nitrogen background pressure of ~ 2.7×10⁴ Pa. Samples processed at ns laser fluences of 1.8 J/cm² or lower do not show any peak corresponding to NbN_x in the XRD patterns. Samples processed at laser fluences above 1.8 J/cm² show XRD peaks of

cubic δ -NbN with (111), (200) and (220) orientations. The other two peaks at 33.43° and 43.68° may be attributed to α -NbN with (633) and (930) orientations or another high order phase like γ -Nb₄N₃ [21]. The peaks from the cubic phase showed slight increases in their intensities as the laser fluence was increased to 5.0 J/cm^2 . The appearance of δ -NbN in the samples is consistent with previous work on laser nitridation of Nb by Nd:YAG laser [11].

The texture coefficient (TC) was calculated from XRD data using the Harris method [22],

$$TC(hkl) = \frac{I(h_i k_i l_i)}{I_o(h_i k_i l_i)} \left\{ \frac{1}{n} \sum_{j=1}^n \frac{I(h_j k_j l_j)}{I_o(h_j k_j l_j)} \right\}^{-1}$$

where $I_o(h_i k_i l_i)$ are intensities of the $(h_i k_i l_i)$ lattice plane of a standard (JSPDS) sample, $I(h_i k_i l_i)$ are the integrated intensities of $(h_i k_i l_i)$ lattice planes under analysis, and n is the total number of reflections used in the calculations. Table 1 shows the texture coefficient calculated for the cubic δ -NbN phase in samples prepared at different ns laser fluences. The texture coefficient shows the change from predominantly (200) texture to (220) as the laser fluence is increased. XRD patterns in Figure 3 show slight changes in the crystal structure of samples prepared at different laser fluences. Small shifts are noted in the (200) peak from 41.55° to 41.16° for a laser fluence of 3.6 and 4.0 J/cm^2 , respectively, while the (220) peak shifts from 60.33° to 59.73° at the same laser fluence. The height of the sample surface was precisely adjusted in each measurement to avoid any possible peak shifts introduced by variation in sample height. The observed shifts may be due to residual stresses that increase with the increase in the laser fluence. Also, a peak shift is expected as other phases develop with the increase in laser fluence, as shown in Figure 3. The mean crystallite size and lattice parameters for the cubic phase of the samples prepared at different laser fluences are shown in Figure 4(a). The crystallite size

of 4.5 – 7.5 nm was calculated from the XRD peaks using the Scherrer equation. The overall behavior of crystallite size is that it increases with increasing laser fluence for the ns laser. Increasing the laser fluence also results in higher XRD peaks, which is an indication of larger crystallites. Changes in the lattice parameter of NbN_x were previously attributed to the formation of nitrogen and/or niobium vacancies, which cause distortion of the crystal lattice [24]. The lattice parameter of the cubic phase was reported to decrease when the N/Nb ratio deviated from unity [24]. For laser fluences higher than 3.6 J/cm^2 , the Bragg peaks shift to lower values due to the increase in the lattice parameter. Figure 4(b) shows the N/Nb ratio obtained from EPMA measurements of samples prepared at different laser fluences. The nitrogen contents in the samples increase as the laser fluence was increased from 1.8 to 4.6 J/cm^2 . Then, the N/Nb ratio decreases as the laser fluence was increased further to 5.0 J/cm^2 , as shown in Figure 4(b). The decrease in the N/Nb ratio at higher laser fluences could be due to ablation of the nitride layer with subsequent laser pulses.

The X-ray diffraction patterns corresponding to the NbN_x films grown by femtosecond laser nitridation with different laser fluences at a constant nitrogen pressure of $4.0 \times 10^4 \text{ Pa}$ are shown in Figure 5. The XRD peaks from the Nb substrate correspond to (110), (200) and (211) orders. From Figure 5, NbN_x starts to form at laser fluences as low as $\sim 0.1 \text{ mJ/cm}^2$. The NbN_x films that are processed at a laser fluence of 0.3 mJ/cm^2 and higher have mixed phases of δ , β and α . The cubic δ -NbN structure starts to appear at a laser fluence $\sim 0.1 \text{ mJ/cm}^2$, showing (111), (200) and (220) diffraction peaks in the XRD pattern. The intensities of these three peaks increase as the laser fluence is increased. The peaks from the δ -NbN are dominant over peaks of the other two phases. With an increase in the laser fluence, there are no shifts observed in the position of the XRD peaks; however, a systematic increase in the intensity of the XRD peaks is

observed. The texture coefficient of the δ -phase for fs laser nitridation is given in Table 2, which shows that the (111) orientation was predominant for laser fluences from 0.3 to 1.3 mJ/cm². In the XRD patterns in Fig. 5, the β -Nb₂N(100) peak overlaps with the α -NbN(633) peak.

Figure 6(a) shows that the mean crystallite size of the δ -phase increases from 3 to 7 nm as the laser fluence is increased from 0.1 to 1.3 mJ/cm². The narrowing of the XRD peaks with the increase in the laser fluence indicates a corresponding increase in the crystallite size. The lattice parameter of the δ -phase decreased from 0.448 to 0.433 nm as the laser fluence was increased from 0.1 to 0.2 mJ/cm², and for higher laser fluences, it had a value almost the same as that at 0.2 mJ/cm². The c/a ratio of the hexagonal β -Nb₂N phase increases with the laser fluence. The c/a ratios were calculated from the (100), (102) and (103) peaks of β -Nb₂N. A similar trend was reported for NbN_x films prepared at different laser fluences [23]. The minimum appears in the lattice parameter of the cubic phase at 0.3 J/cm² and can be explained in light of the change in phases of formed NbN_x layer. Laser fluences higher than 0.3 J/cm² cause the formation of the cubic phase along with the other peaks of the β -Nb₂N hexagonal phase. This is consistent with the observation that for the NbN_x films the phases are a mixture of cubic and hexagonal phases with the ratio of hexagonal-to-cubic phases dependent on the laser fluence [23]. Figure 6(b) shows the EPMA results for the nitrogen-to-niobium ratio (N/Nb) in the samples prepared by fs laser nitridation at different laser fluences. The N/Nb increases as the laser fluence is increased. The corresponding XRD patterns of these samples, Figure 5, show increased peaks of NbN_x with increased laser fluence, which is consistent with the increased nitrogen content observed in the EPMA measurements. The N/Nb ratio increased to ~ 0.47 as the laser fluence was increased to 0.4 mJ/cm², then it stayed around this value as the laser fluence was increased further to 1.3 mJ/cm². These values are far below the results we obtained for nitridation with the ns laser

shown in Figure 4(b). This may be due to the high repetition rate of the fs laser source (1 kHz for fs versus 10 Hz for ns) that causes more than one laser pulse to hit the same spot on the surface of the sample many times, ablating some of the formed NbN_x and making it Nb rich. The almost constant N/Nb ratio in the EPMA results of fs laser nitridation at these higher laser fluences indicates that the nitridation process reaches a steady-state value due to a balance between NbN_x generation and its ablation by subsequent pulses.

In fs laser nitridation, the lattice is heated on a picosecond time scale, causing a direct solid to vapor transition, resulting in plasma formation [25]. In the case of ns laser nitridation, the heating time is long enough to cause melting of the surface, followed by evaporation from the liquid melt. For fs laser, the ablation depth is strongly dependent on the laser fluence [25]. As the laser fluence is increased, the ablation depth increases with an associated increase in plasma density. Higher plasma density could promote the formation of more NbN_x phases than that observed in ns laser nitridation, such as the $\beta\text{-Nb}_2\text{N}$ phase observed in the XRD patterns in Figure 5.

The formation of different phases for processing with different lasers and laser fluences can be related to the heat diffusion. For pulsed laser surface heating and considering a two-dimensional heat diffusion model, the heat diffusion length is $l = \sqrt{D\tau}$, where D is the diffusion coefficient of the material and τ is the laser pulse width. For equal fluences and strongly absorbing materials, as in the case of metals, when the laser pulse is reduced, the diffusion length is also reduced, resulting in increased surface temperature for a constant laser fluence. The maximum surface temperature increases rapidly as the laser pulses become shorter than 1 ps [26]. As pulse duration decreases, the energy is absorbed to form vapor or cause superheating of the liquid. For fs laser pulses (≤ 100 fs), the pulses are short enough not to be absorbed by the

vapor. For longer pulses (>100 ps), more time is available for the heat to diffuse into the bulk before the vapor is formed [26]. That significantly affects the type of nitride phases formed and their orientations on the surface.

3.3. Surface morphology

The surface morphology of the laser-treated Nb was studied by scanning electron microscopy and atomic force microscopy. Figure 7 shows SEM images of ns laser treated surfaces along with an untreated Nb sample (Figure 7(a)). The laser fluence was varied, while the nitrogen background pressure was kept at 2.7×10^4 Pa. Figure 7(b) shows a noticeable change in surface morphology from this in Figure 7(a) which indicates surface melting at a laser fluence of 1.8 J/cm^2 . Further increase in the laser fluence results in an increase in surface roughness. At a laser fluence of $\geq 1.8 \text{ J/cm}^2$, the formation of melt splash is observed as the laser expels the melt, resulting in increased surface roughness. Microcracks are also observed on the surface of samples, which may be due to the greater quench rate and development of thermal stress. In the case of fs laser nitridation, the heat conduction is negligible and, thus, thermal damage which causes microcracks is greatly reduced. [27]. Comparing surface roughness of NbN_x samples obtained by thermal treatment in nitrogen background gas, one finds that the laser nitridation causes higher roughness. For samples prepared by pulsed laser ablation, surface roughness increases as the laser fluence is increased. If the laser pulses interacting with the surface are well-seperated, by increasing the scanning speed or decreasing the laser repetition rate, that could lead to less surface roughness.

Figure 8 shows SEM images of fs laser heated samples done at different laser fluences. The SEM images of the samples show that the surface is uniformly covered with laser induced

ripples forming periodic structure. For the ripple pattern oriented parallel to the beam polarization, the average ripple spacing (Λ) can be calculated by the following formula [28, 29]:

$$\Lambda = \frac{\lambda}{\cos \theta}$$

where λ is the wavelength of laser light and θ is the light incident angle measured with respect to the surface normal. The ripple spacing value calculated using $\lambda = 800$ nm and $\theta = 45^\circ$ gives 1.13 μm , which is close to the 1.10 – 1.26 μm measured from the SEM images of Figure 8. Figure 9 shows that the ripple period slightly increases with the laser fluence. The morphology of the surface depends significantly on the laser fluence. As the laser fluence is increased, the density of grains and surface roughness increase, as observed in Figure 10. The small changes in ripple spacing as the laser fluence was increased can be attributed to change in the surface roughness. Previous studies showed that the surface roughness plays an important role in determining the morphology of the periodic pattern [30]. It was previously reported that as the surface roughness of the samples becomes larger, a small or no change occurs in the ripple periodicity [31]. Laser heating of the Nb substrates causes an increase in surface roughness for both samples prepared by ns and fs lasers.

Figure 10 shows cross-sectional SEM images of laser treated samples milled by a focused ion beam (FIB). Figure 10(a) is for the sample processed with the ns laser at 3.6 J/cm², while for Figure 10(b) the sample was processed with the fs laser at 0.7 mJ/cm². The thickness of the nitride layer was about 330±25 nm for (a) and 450±65 nm for (b). The cross-section SEM images show that the laser nitridation of the surface is not uniform with micron-sized peaks and valleys. The formation of nonuniform thickness of the NbN_x layer in fs laser pulses, as shown in Figure 10(b), can be due to an overlap of the high repetition rate (1 kHz) fs laser pulses. The

overlap of laser pulses results in successive ablation pulses interacting with the same region causing ablation that depends on the surface condition prepared by the previous pulse. Figure 10(c) shows the root mean square (RMS) roughness obtained from AFM images of the ns laser heated samples. The measurements show increases in surface roughness with the laser fluence. The RMS of the samples' surfaces increases from 83 nm at 1.8 J/cm^2 to 323 nm at 4.6 J/cm^2 , then decreases to 208 nm as the laser fluence was increased to 5.0 J/cm^2 . The reduction of surface roughness at the highest laser fluence used (5.0 J/cm^2) could be due to variations in roughness at different locations for the samples processed at 4.6 and 5.0 J/cm^2 , and the roughness could be reaching a saturation level. For the fs laser processed samples, the surface roughness did not show dependence on the laser fluence and was $50 - 55 \text{ nm}$. The increase in surface roughness with the laser fluence for the ns laser processed samples is expected when the laser fluence is higher than that required for melting, due to increased ablation and splashing of the melt [8]. Similar observation was reported previously [11].

4. Conclusion

The NbN_x samples prepared by ns laser nitridation had δ -NbN structure for laser fluences higher than 1.8 J/cm^2 . The SEM images showed surface melting and increased crack formation as the laser fluence was increased. For fs laser nitridation, NbN_x starts to form at a laser fluence of $\sim 0.1 \text{ mJ/cm}^2$. The NbN_x films formed at a laser fluence of 0.3 mJ/cm^2 and higher have δ , β and α phases. The cubic δ -NbN structure is dominant over the other phases. The results of laser nitridation, both with the ns and fs lasers, are in sharp contrast with nitridation by thermally heating Nb in a nitrogen atmosphere; in thermal nitridation at temperatures up to 900°C , only the hexagonal β - Nb_2N phase was detected [20]. The differences in the structures formed is due to

the higher surface temperatures achieved with laser nitridation, interactions of the laser pulses with the formed nitride, and the fast temperature quench rate. The formation of oxides is also confirmed by XANES measurements at the O K edge and the oxide layer is found to be Nb_2O_5 on the surface of the samples.

In summary, we have shown that the laser fluence and pulse width plays a crucial role in determining the phase and composition of the NbN_x films. The results showed NbN_x layers predominantly of the cubic $\delta\text{-NbN}$ phase; which is of interest for use in SRF cavities. Laser nitriding of Nb offers an alternative to thermal nitridation and provides some control on the phase and morphology of the formed NbN_x . Laser nitridation can be scaled to large surface. Contrary to vapor-phase deposition techniques, such as in sputtering and pulsed laser deposition, laser nitridation can be used to nitride geometrically complex surfaces using laser delivery methods such as fiber optics and galvanometers.

Acknowledgements

This work was partially supported by the National Science Foundation Grant Nos. 0821180 and 1228228. A. H. F. Was supported by a Jefferson Lab scholarship. The authors are grateful to the Stanford Synchrotron Radiation Lightsource (SSRL), California, USA, for providing synchrotron-based XAS facility. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. Support of DOE Cooperative Research Program for SESAME project is acknowledged by A.H.F, O.M.O and Y.U.

5. References

- [1] M. Faucher, T. Fournier, B. Pannetier, C. Thirion, W. Wernsdorfer, J. C. Villegier, V. Bouchiat, *Physica C*, 368 (2002) 211–217.
- [2] C. Benvenuti, P. Chiggiato, L. Parrini, R. Russo, *Nucl. Instrum. and Meth. in Phys. Res., Sect. A*, 336 (1993) 16–22.
- [3] J. R. Gao, M. Hajenius, F. D. Tichelaar, T. M. Klapwijk, B. Voronov, E. Grishin, G. Gol'tsman, C. A. Zorman, M. Mehregany, *Appl. Phys. Lett.*, 91 (2007) 062504-062507.
- [4] A. Gaggero, S. J. Nejad, F. Marsili, F. Mattioli, R. Leoni, D. Bitauld, D. Sahin, G.J. Hamhuis, R. Notzel, R. Sanjines, A. Fiore, *Appl. Phys. Lett.*, 97 (2010) 151108-151111.
- [5] R. Musenich, P. Fabbriatore, G. Gemme, R. Parodi, M. Viviani, B. Zhang, V. Buscaglia, C. Bottino, *J. Alloys Comp.*, 209 (1994) 319–328.
- [6] E. Carpena, P. Schaaf, M. Han, K.P. Lieb, M. D. Shinn, *Appl. Surf. Sci.*, 186 (2002) 195–199.
- [7] P. Schaaf, *Prog. in Mater. Sci.* 47 (2002) 1-161.
- [8] S. Singaravelu, J.M. Klopff, C. Xu, G. Krafft, M. J. Kelley, *J. Vac. Sci. Technol., B*, 30 (2012) 051806-051813.
- [9] P. Kneisel, G. Ciovati, J. Sekutowicz, L. Turlington, *IEEE Trans. Appl. Supercond.*, 19 (2009) 1416–1418.
- [10] J. Halbritter, *J. Appl. Phys.*, 97 (2005) 083904-083916.
- [11] S. Singaravelu, J. M. Klopff, G. Krafft, M.J. Kelley, *J. Vac. Sci. Technol., B*, 29 (2011) 061803-061809.
- [12] H. Padamsee, J. Knobloch, T. Hays, *RF superconductivity for accelerators*, Wiley-VCH, 2008.
- [13] B. T. Thole, G. van der Laan, *Phys. Rev. B*, 38 (1988) 3158–3171.
- [14] T. K. Sham, *Phys. Rev. B* 31 (1985)1888-1902.
- [15] K. Hirsch, V. Zamudio-Bayer, J. Rittmann, A. Langenberg, M. Vogel, T. Möller, B.V. Issendorff, and J. T. Lau, *Phys. Rev. B*, 86 (2012) 165402-165413.
- [16] D. Bach, R. Schneider, D. Gerthsen, J. Verbeeck, W. Sigle, *Microsc. Microanal.*, 15 (2009) 505–523.
- [17] D. Bach, R. Schneider, D. Gerthsen, *Microsc. Microanal.*, 15 (2009) 524–538.
- [18] D. Bach, H. Stormer, R. Schneider, D. Gerthsen, J. Verbeeck, *Microsc. Microanal.*, 12 (2006) 416–423.
- [19] R. Tao, R. Todorovic, J. Liu, R. J. Meyer, A. Arnold, W. Walkosz, P. Zapol, A. Romanenko, L. D. Cooley, R. F. Klie, *J. Appl. Phys.* 110 (2011) 124313-124321.
- [20] Y. Ufuktepe, A. H. Farha, S.Kimura, T. Hajiri, F. Karadağ, Md A. Al Mamun, A. A. Elmustafa, G. Myneni, and H. E. Elsayed-Ali, *Mater. Chem. Phys.* 141 (2013) 393–400.
- [21] Powder Diffraction File, 01-071-0096, PDF-2/Release 2004, 2004.
- [22] C. S. Barrett and T. B. Massalski, *Structure of Metals*, Pergamon Press, Oxford, third edition 1980.
- [23] A. H. Farha, A.O. Er, Y. Ufuktepe, H.E. Elsayed-Ali, *Mater. Chem. Phys.*, 132 (2012) 667–672.
- [24] A. V. Linde, R. M. Marin-Ayral, D. Granier, F. Bosc-Rouessac, V. V. Grachev, *Mater. Res. Bull.*, 44 (2009) 1025–1030.
- [25] B. N. Chichkov, C. Momma, S. Nolte, F. Alvensleben, A. Tünnermann, *Appl. Phys. A*, 63 (1996) 109–115.

- [26] P. P. Pronko, S. K. Dutta, D. Du, R. K. Singh, J. Appl. Phys., 78 (1995) 6233–6240.
- [27] J. P. Ulerich, L. C. Ionescu, J. Chen, W. O. Soboyejo, C. B. Arnold, in *Proc. SPIE* 6458, Photon Processing in Microelectronics and Photonics VI, (2007) 645819-645829.
- [28] J. E. Sipe, J. F. Young, J. S. Preston, H. M. van Driel, Phys. Rev. B, 27 (1983) 1141–1154.
- [29] F. Costache, M. Henyk, J. Reif, Appl. Surf. Sci., 208–209 (2003) 486–491.
- [30] J. F. Young, J. S. Preston, H. M. van Driel, J. E. Sipe, Phys. Rev. B, 27 (1983) 1155–1172.
- [31] Y. Yang, J. Yang, L. Xue, Y. Guo, Appl. Phys. Lett., 97 (2010) 141101-141104.

Table captions:

Table 1: Texture coefficients of the cubic δ -NbN phase in ns laser heated NbN_x samples at different laser fluences.

Table 2: Texture coefficients of the cubic δ -NbN phase in fs laser heated NbN_x samples at different laser fluences.

Table 1:

Laser Fluence, (J/cm ²)	TC(111)	TC(200)	TC(220)
5.0	0.93	1.01	1.06
4.6	0.92	1.01	1.07
4.0	1.12	0.55	1.33
3.6	0.79	1.00	1.21
3.0	0.99	1.00	1.00
2.4	1.05	1.44	0.51
1.8	0.89	1.38	0.73

Table 2:

Laser Fluence, mJ/cm ²	TC(111)	TC(200)	TC(220)
1.3	1.11	0.80	1.08
1.1	1.15	0.81	1.04
0.7	1.07	0.93	0.99
0.4	1.21	0.92	0.87
0.3	1.17	1.09	0.74

Figure captions:

Figure 1: XANES results of NbN_x surface for samples processed by the ns laser at different fluences: (a) XANES measured at the Nb-M_{2,3} edges. (b) Normalized peak intensity ratio of M₃ to M₂+M₃. The intensity ratios calculated from the integrated area under each peak in (a). (c) Oxygen 1s X-ray absorption spectra of NbN_x surface layers prepared by ns laser. Laser fluences in mJ/cm² are given at the side of each curve.

Figure 2: XANES results of NbN_x surface for samples processed by the fs laser at different laser fluences: (a) XANES at the Nb-M_{2,3} edges. (b) Normalized peak intensity ratio of M₃ to M₂+M₃. The intensity ratios calculated from the integrated area under each peak in (a). (c) Oxygen 1s X-ray absorption spectra of NbN_x thin films prepared by fs laser at different laser fluences.

Figure 3: XRD patterns for samples prepared at different ns laser fluences at the same nitrogen pressure of 2.7x10⁴ Pa.

Figure 4: (a) Variation of crystallite size and lattice parameter of the cubic δ-NbN phase with ns laser fluences. (b) EPMA measurement shows N/Nb ratio for samples processed at different ns laser fluences. The error bars represent the standard deviations calculated from the three cubic δ-NbN with (111), (200) and (220) orientations. The error bars represent the standard deviations calculated for measurements done at five different points on each sample. The solid lines are drawn as a guide for the eye.

Figure 5: XRD patterns for NbN_x samples processed by fs laser at different laser fluences.

Figure 6: (a) Crystallite size and lattice parameter of the (200) peak of the cubic δ-phase. (b) EPMA measurement shows N/Nb ratio for samples processed at different fs laser fluences. The error bars in both the crystallite size and lattice constant represent the standard deviations calculated from the XRD data of the three cubic δ-NbN peaks from the (111), (200) and (220) planes. The error bars in the EPMA measurements represent the standard deviation calculated from measurements at five different points on each sample. The solid lines are drawn as a guide for the eye.

Figure 7: SEM images (X6, 000) of the NbN_x surface layer produced by the ns laser at different fluences: (a) bare Nb, (b) 1.8 J/cm², (c) 2.4 J/cm², (d) 3.0 J/cm², (e) 3.6 J/cm² (f) 4.0 J/cm², (g) 4.6 J/cm², and (h) 5.0 J/cm².

Figure 8: SEM images (X6,000) of the NbN_x surface layer produced by the fs laser at different fluences: (a) 0.1 mJ/cm², (b) 0.2 mJ/cm², (c) 0.3 mJ/cm², (d) 0.4 mJ/cm² (e) 0.7 mJ/cm² and (f) 1.1 mJ/cm².

Figure 9: The dependence of the ripple periodicity on the laser fluence for NbN_x samples processed by fs laser. The error bars represent the standard deviations calculated from spacing measurements done at different locations on each SEM image.

Figure 10: Cross section SEM images of the NbN_x laser processed samples for (a) ns laser at 3.6 J/cm² and (b) fs laser at 0.7 mJ/cm² laser fluence. (c) The measured surface roughness for different laser fluences for ns laser processed samples.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10