



## Effects of substrate temperature on properties of NbN<sub>x</sub> films grown on Nb by pulsed laser deposition

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### ABSTRACT

NbN<sub>x</sub> films were deposited on Nb substrate using pulsed laser deposition. The effects of substrate deposition temperature, from room temperature to 950 °C, on the preferred orientation, phase, and surface properties of NbN<sub>x</sub> films were studied by X-ray diffraction, atomic force microscopy, and electron probe micro analyzer. We find that the substrate temperature is a critical factor in determining the phase of the NbN<sub>x</sub> films. For a substrate temperature up to 450 °C the film showed poor crystalline quality. With temperature increase the film became textured and for a substrate temperature of 650–850 °C, mix of cubic δ-NbN and hexagonal phases (β-Nb<sub>2</sub>N + δ'-NbN) were formed. Films with a mainly β-Nb<sub>2</sub>N hexagonal phase were obtained at deposition temperature above 850 °C. The *c/a* ratio of β-Nb<sub>2</sub>N hexagonal shows an increase with increased nitrogen content. The surface roughness of the NbN<sub>x</sub> films increased as the temperature was raised from 450 to 850 °C.

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### 1. Introduction

Transition metal nitrides are well known for possessing a number of extreme properties [1]. Among the nitride coatings that are of increasing interest is niobium nitride (NbN<sub>x</sub>), because of its excellent physical properties, such as high hardness [2], wear resistance [3], and superconductivity [4]. Cubic δ-NbN has a superconducting transition temperature of 17.8 K, compared with 9.2 K for pure Nb [5]. The phase and preferred orientation of the film strongly depend on preparation parameters as well as the deposition methods. The preferred orientation in transition metal nitrides affects many processes, such as carrier diffusion in microelectronic devices, the wear resistance of tool coatings, the corrosion resistance of the coating, and in the case of NbN<sub>x</sub>, its superconducting properties. The superconducting properties of NbN<sub>x</sub> are strongly affected by Nb–N

composition and crystal structure. Hence, controlling the phase and crystal structure of NbN<sub>x</sub> is important for many applications.

NbN<sub>x</sub> crystallizes in several phases and in most cases the NbN<sub>x</sub> films are present in a mixed phase composition [6,7]. NbN<sub>x</sub> exists in different crystal structures, including β-Nb<sub>2</sub>N (hexagonal), γ-Nb<sub>4</sub>N<sub>3</sub> (tetragonal), δ-NbN (face-centred cubic), δ'-NbN (hexagonal), ε-NbN (hexagonal), and η-NbN (hexagonal). It is reported that the hexagonal phases (β-Nb<sub>2</sub>N, δ'-NbN) exhibit significantly higher hardness values compared to that of the cubic phases [8]. Therefore, the investigations of the structural properties of the hexagonal phases are of particular interest.

Different deposition techniques have been used to obtain NbN<sub>x</sub> thin films, such as reactive magnetron sputtering [9,10], ion beam assisted deposition [11,12], filtered arc deposition [13], and pulsed laser deposition (PLD) [14,15]. Pulsed laser deposition method is a highly flexible thin-film growth technique. For PLD, the composition and structural properties of NbN<sub>x</sub> films are mainly influenced by nitrogen pressure, laser power, and substrate deposition temperature. There have been many reports about NbN<sub>x</sub> thin films on

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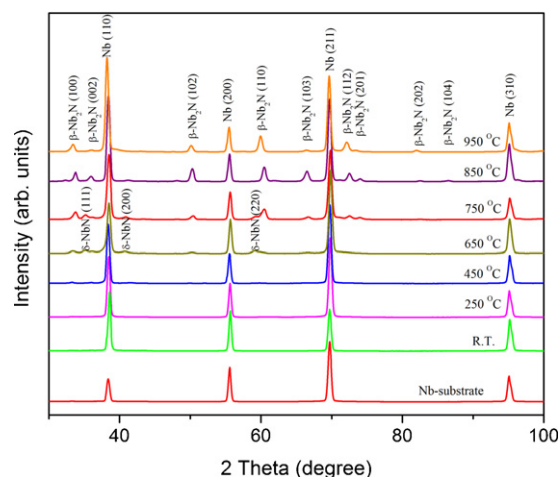
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MgO and Si substrates fabricated by PLD discussing the influence of the deposition parameters, such as background gas pressure and substrate temperature, on the structure of the film [16–20]. To the best of our knowledge, no comparable work has been done on the crystallographic structure of  $\text{NbN}_x$  coatings deposited on Nb substrates by PLD. The production of  $\text{NbN}_x$  thin films on Nb substrate is especially important in high-energy physics experiments and it can be used for high electric field superconducting radio frequency cavities. The previous studies on  $\text{NbN}_x$  prepared by PLD have revealed that the  $\text{NbN}_x$  shows non-stoichiometry and phase change with increasing nitrogen content in the film [14,15]. It is important to obtain high-quality  $\text{NbN}_x$  coatings on Nb, especially for radio frequency cavities for potential applications in increasing surface hardness or providing a barrier layer for hydrogen diffusion into Nb. We performed a series of experiments to investigate formation of  $\text{NbN}_x$  on Nb in the temperature range from room temperature to 950 °C by PLD. The formation of different phases at various deposition temperatures and their influence on the morphology and crystal structure were investigated.

## 2. Experimental

$\text{NbN}_x$  films were grown on Nb single-crystal substrate by ablating Nb target. The chamber was equipped with a turbo-molecular and ion pump operated at a base pressure of  $\sim 1 \times 10^{-9}$  Torr at room temperature. A pulsed Nd:YAG laser (wavelength  $\lambda = 1064$  nm, repetition rate 10 Hz, pulse duration  $\sim 40$  ns) was focused with a 50 cm focal length lens at 45° onto a rotating (25 rpm) Nb metal target (99.995% pure). The input pressure of the ambient nitrogen gas was controlled by a high-precision leak valve and measured with a convectron gauge. The nitrogen operating pressure was achieved by filling the vacuum chamber with the right amount of gas (99.999% pure) and keeping it in static condition. The samples (8.6 mm  $\times$  6.6 mm  $\times$  0.7 mm) were cut by wire electro-discharge machining from an Nb slice of ingot “H” from the company (CBMM), Brazil. The residual resistivity ratio of this ingot is about 200. Before cutting the samples, the surface of the Nb slice was mechanically polished with  $\text{Al}_2\text{O}_3$  abrasive disks. The Nb slice from the ingot has large grains (several  $\text{cm}^2$  areas); therefore, the samples were either single crystals or had a single grain boundary. The samples were etched by the buffered chemical polishing (BCP) method [21]. The BCP solutions (1:1:1 and 2:1:1  $\text{HPO}_3:\text{HNO}_3:\text{HF}$ ) were cooled down to 10 °C during the cleaning process. Approximately a 50 micron layer of material was removed by BCP that resulted in Nb substrates with root-mean square (RMS) surface roughness about 0.6 nm for  $2 \mu\text{m} \times 2 \mu\text{m}$  scan area, determined by atomic force microscope (AFM). The etched samples were rinsed in deionized water, dried under nitrogen flow, and then degassed for several hours at  $\sim 800$  °C in the ultrahigh vacuum (UHV) chamber under a base pressure of  $\sim 1 \times 10^{-9}$  Torr before starting PLD. X-ray diffraction (XRD) of cleaned Nb substrate indicates that most crystalline grains of Nb substrate exhibit crystallographic Nb (110), (200), (211), and (310) orientations [22]. After BCP and rinsing with deionized water, the substrates were attached to the substrate heater with tungsten wire and held  $\sim 6$  cm from the target.

Different substrate temperatures were used for deposition. The substrate temperature was measured using a chromel–alumel (K-type) thermocouple that was mechanically attached to the substrate surface. The thermocouple calibration was checked before installing it into the UHV chamber, using the boiling point temperature of water. In order to obtain accurate temperature values, first we carried out relating the current–voltage calibration curve from the heater to the substrate surface temperature. We can measure temperature reproducibly and with an estimated accuracy of  $\pm 20$  °C at 250 °C and  $\pm 50$  °C at 950 °C; this accuracy is limited by the



**Fig. 1.** XRD patterns of  $\text{NbN}_x$  thin films deposited on Nb substrate at different temperatures. The XRD pattern of the Nb substrate is also shown. For a substrate temperature up to 450 °C, the film shows poor crystalline quality. With temperature increase, the film becomes textured and for a substrate temperature of 650–850 °C, mix of cubic  $\delta$ - $\text{NbN}$  and hexagonal phases ( $\beta$ - $\text{Nb}_2\text{N}$  +  $\delta'$ - $\text{NbN}$ ) are formed.

sample contact to the heater surface and the temperature gradient across the heater. The thickness of the PLD grown films is about 45 nm as calibrated by conducting similar deposition conditions on silicon substrate followed by cross-sectional scanning electron microscopy (SEM) measurements. A JEOL JSM-6060 LV SEM was used for these cross-sectional measurements. As soon as the deposition was completed, the heater was turned off and the sample was left to cool down for several hours under UHV. The deposition was performed for 1 h.

XRD measurements were made using graphite-monochromated  $\text{CuK}\alpha$  radiation on a Bruker-AXS three-circle diffractometer, equipped with a SMART Apex II CCD detector. The films were identified in the symmetric  $\theta/2\theta$  geometry, ranging from  $2\theta = 30^\circ$  to  $100^\circ$ . The chemical composition ( $\text{N}/\text{Nb} = x$ ) of the  $\text{NbN}_x$  samples was determined by a Cameca SX100 electron probe micro analyzer (EPMA).

The concentration of the A phase in an A + B mixed phase film was calculated by the following formula:

$$A[\%] = \frac{\sum I_A}{\sum I_A + \sum I_B} \quad (1)$$

where  $\sum I_A$  and  $\sum I_B$  are the sum of the intensities of A phase and B phase peaks in the measured XRD patterns. The morphology of films was observed using a Digital Instruments Dimension 3100 AFM. All AFM images were taken in air using tapping mode. SEM images were taken at an accelerating voltage of 30 kV. The films were deposited at different substrate deposition temperatures from room temperature to 950 °C under constant values of nitrogen pressure and laser energy density of 100 mTorr and  $\sim 15$  J/cm<sup>2</sup>, respectively.

## 3. Results and discussion

Fig. 1 shows XRD patterns of  $\text{NbN}_x$  films on Nb prepared at different substrate deposition temperatures. The XRD pattern of the Nb substrate is also included in Fig. 1 as a reference. Diffraction peak assignments are indicated. The films grown at room temperature and 250 °C showed poor crystalline qualities, while increasing the substrate temperature resulted in better crystallization. As the temperature was increased from 450 to 650 °C, the films became highly textured and can be indexed with a mixture of cubic and hexagonal phases. Previous work showed that  $\text{NbN}_x$  films formed in cubic

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