High Quality Ultrathin NbN Layers On Sapphire for Superconducting Single Photon Detectors

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Abstract. Ultra-thin epitaxial NbN layers are a key component of Superconducting Single Photon infrared Detectors. Efforts devoted to the layer growth aim at improving their critical temperature and critical current density, while keeping their thickness close to 5 nm and Tc above 10 K, which insure a large bandwidth, large SNR detection at 4K. Choice of substrate is critical: for both applications, MgO wafers and R-plane sapphire are usually considered as best substrates to grown onto. However, growing NbN on M-plane orientation of sapphire wafer, 3 inch in diameter, can help improving the film quality and fabrication yield. NbN thin films were grown by reactive DC magnetron sputtering at about 600°C and passivated by an AlN layer 1.5nm thick deposited in-situ at room temperature. Growth on M-plane is shown to be better than on other sapphire orientations, including R-plane: NbN layer critical temperature reaches 13.3 K, uniform on the wafer, for a film thickness of 4.4nm measured by X-ray reflectivity. Transport properties of NbN grown on those various substrates have been correlated to their crystallographic microstructure, examined by both symmetric and asymmetric X ray diffraction. Observation of diffraction peaks has given insight on the disorientation of the NbN film.

1. Introduction
Superconducting Single Photon Detectors (SSPD) [1] have encountered a growing interest in the past few years. Those detectors basically consist of a superconducting nanowire biased near its critical current. The absorption of a photon produces a normal hot spot that grows until a resistive section is formed across the wire, thus generating a detectable voltage pulse. Single photons can be detected with an efficiency reaching 57 % [2]. The reset time in the order of a nanosecond [3] allows counting rates of several hundreds MHz, while preserving a very low noise equivalent power. By providing a means to efficiently detect a single photon in a large spectral window (visible to IR), they are a preferred choice for quantum cryptography systems, and also offer alternatives in applications dealing with fast, low intensity signals, e.g. IC failure testing.
Thanks to its superconducting properties at rather high temperature (bulk \( T_c = 17 \) K), niobium nitride (NbN) is a material of choice for single photon detection applications. SSPDs are commonly made by patterning the detector structure in an ultrathin (typically 5 nm) film deposited on R plane sapphire (R-Al\(_2\)O\(_3\)). The demand for high quality NbN has therefore encountered a renewed interest in the last 10 years. Heteroepitaxial NbN can be grown on various substrates: MgO [4,5], sapphire [5], and semiconductors with a buffer layer [6], and more recently 3C-SiC/Si [7]. The epitaxial growth is conveniently achieved by reactive magnetron sputtering at temperatures between 300 and 1500 K. Up to now, growth on MgO gives the best \( T_c \) and lowest resistivity, e.g. \( T_c = 12 \) K and \( \rho_{20K} = 120 \) \( \mu \Omega \cdot \text{cm} \) for a 4 nm thick film grown at room temperature [4,8,9], thanks to a low lattice mismatch and a defect free substrate. However, MgO substrates are expensive and hydrophilic, whereas the here studied sapphire substrates are expensive and hydrophilic, whereas the here studied sapphire substrates are chemically inert and enable a large scale deposition.

We show here that a proper choice of the orientation of the sapphire substrate helps improving the crystalline quality of the NbN layer, and hence its superconducting properties. Electrical transport properties are compared to structural characteristics. Texture of grown films is evidenced by pole figures, and their mosaicity, measured with the help of asymmetric X-ray diffraction, is shown to be dominated by tilt and twist.

2. Experimental

NbN films were grown at CEA-DRFMC by DC magnetron sputtering of a Nb target in a Ar/N\(_2\) plasma [10]. Very thin films were deposited at 600 °C substrate temperature and passivated by an AlN layer in-situ deposited at room temperature [11]. Deposition was conducted on whole 3 to 4 inch diameter wafers of differing orientations (A, M, and R), supplied by Kyocera. The NbN layer thicknesses were measured by X-ray reflectometry, using a Philips X’Pert for the data acquisition and a Paratt formalism [12] to fit the experimental data. The crystalline texture characterizations was done by X-ray diffraction using a Cu K\( \alpha \) source within a texture apparatus (Siefert) in the Schulz configuration. The very low noise level allowed working on very thin films. In the following, we refer to \( \chi \) as the tilt angle of the sample with respect to X-ray diffusion vector (horizontal) and \( \phi \) as the azimuthal rotation angle (around the normal to the sample). Pole figures were acquired using RayleX software. The X-Ray diffraction measurements were performed using a high resolution Seifert XRD 3003 PTS-HR diffractometer. Due to signal weakness, we used a low resolution mode which consists of a mirror (for parallelizing the beam) prior to a two-reflection (220) Germanium Bartels (only one of the two Germanium monochromators was used), and Soller slits before the detector. In this configuration, the full width at half maximum (FWHM) of the direct beam is 0.08°, and the omega resolution 0.045°. Resistance as a function of temperature (2 – 300 K) was measured by four points measurement in a PPMS from Quantum Design. The critical temperature \( T_c \) was taken as the temperature half-way the superconducting resistive transition.

3. Thin films transport properties

We first studied the electrical properties of NbN films grown on M-plane sapphire (M-Al\(_2\)O\(_3\)) to the ones on R-Al2O3, currently used for SSPD fabrication. Figure 1 shows the room temperature resistivity and the critical temperature obtained for films of different thicknesses (obtained by varying the deposition time), for two substrate orientations. We stress here the importance of a precise thickness determination, which in turn deserves a more detailed presentation below. As expected, the resistivity (resp. critical temperature) is increasing (resp. decreasing) with decreasing thicknesses, i.e. when getting closer to the superconductor-insulator transition.
Figure 1: Room temperature resistivity (squares) and critical temperature (dots) of NbN thin films deposited on 3 to 4 inch sapphire wafers, either R plane (filled symbol) or M plane (open symbol).

Data from a deposition on 2x2cm M-plane sapphire (open stars) shows a slightly degraded performances. Lines are a guide for the eye.

Figure 2: (left) Normalized resistance as a function of temperature for two NbN thin films of two different thicknesses grown on M-Al2O3. (right) Corresponding reflectivity measurement and fitting, as a function of diffusion vector Q (units 2π/λ).

3.1. Thickness measurement

The thickness has been measured by X–ray reflectometry (Figure 2) on every deposited film. For a typical 4 - 6 nm thick samples, the reflectivity oscillations are observed untill an incidence angle 2θ=10-15°, which proves the low roughness of grown films, on an area of about 1mm². It is worth noting here that it is even the case for films as thin as 2.6 nm (8 monolayers). These observations can be quantified by fitting the experimental data with the Paratt formalism. On the one hand, the NbN/sapphire interface is found to be rather sharp (roughness ≈ 1 Å) so that chemical mixing during deposition must be limited, as in the case of the Nb/sapphire interface [13] but in contrast to NbN growth on Si. On the other hand, the roughness of the NbN film is found to be about 3 (resp. 8) Å for a 5 (resp. 12) nm thick film, thus increasing with the thickness of the film. However, the NbN layers on A-plane are rougher than on M- or R- planes, which could be related to the fact that dense (111) planes are perpendicular to the growth direction (see epitaxial relationship details below). Being strained by
the lattice mismatch between NbN and sapphire, the A-plane oriented layers may start relaxing at comparably lower thicknesses than for the other sapphire orientations.

3.2. Choice of sapphire orientation
The choice of sapphire orientation also impacts corresponding electrical transport properties (Figure 1). Resistivity of NbN films grown on M- (and A-plane, data not shown) is 40 % lower ($\rho_{20K} = 110 \mu\Omega\cdot cm$) than that on R-plane ($\rho_{20K} = 180 \mu\Omega\cdot cm$), for identical thickness (4.5 nm). Resistive ratio (RR=$\rho_{300K}/\rho_{20K}$) is also closer to 1 for M-plane (RR=0.95) than for R plane (RR=0.75), which is an indication of higher quality NbN also illustrated by a slightly higher $T_c$ of NbN layers grown on M-plane. Moreover, we have shown elsewhere [14] that critical current density of NbN grown on M plane is 25% higher than that on R plane. The growth of NbN on M-Al2O3 hence provides a material quality comparable to that grown on MgO, offering a new competitive alternative for NbN growth.

4. Structural characterization
The electrical transport properties, particularly resistivity and critical current density, are sensitive to the microstructure of the film. Before focusing on the reciprocal lattice point (RLP) shape, we studied the crystalline orientation of NbN films with respect to the underlying sapphire orientation.

![Figure 3: Pole figure of cubic NbN (111) Bragg reflections. Left: after growth on R plane sapphire ($2\theta=35.03^\circ$), the two twinning variants are noted NbN1 and NbN2. Right: after growth on M plane sapphire ($2\theta=35.24^\circ$). The contour lines underline the weak diffraction signal from NbN.](image)

4.1. Texture comparison of NbN grown on R-Al2O3 and M-Al2O3
The texture of grown thin films was investigated by pole figures. In a previous work [14] using the \{200\} Bragg reflections, we have determined the following epitaxy relationships:

$$\pm\{135\}_{\text{NbN}}//\{10\bar12\}_{\text{Al}_2\text{O}_3} \text{ and } \{1\bar21\}_{\text{NbN}}//\{10\bar11\}_{\text{Al}_2\text{O}_3} \text{ (R-plane)}$$

$$\{110\}_{\{010\}_{\text{NbN}}}//\{001\}_{\text{Al}_2\text{O}_3} \text{ (M-plane)}$$

Pole figures with the help of cubic NbN \{111\} Bragg reflections (Figure 3), in same samples as in Ref. [14] confirms those assignments. Indeed, the diffraction pattern consists of isolated spots that are all indexed according to the above relationships. We do not observe any other minor orientation. We also checked that NbN/R-Al2O3 is twinned, in contrast to the NbN/M-Al2O3. The two twin variants are
symmetrical one to another with respect to the NbN \(\{1\overline{2}1\}\) zone axis, which lies parallel to the Al2O3 \([10\overline{1}1]\) direction. The NbN \([135]\) direction is also slightly disoriented (2°) from the R-plane of sapphire, a fact also observed by closer examination of the position and the shape of Bragg peaks (see below). This tilt cannot be ascribed to the substrate miscut, which was below 0.5°.

4.2. Mosaicity of NbN/Rh-Al2O3
We have studied the microstructure of NbN grown on R-plane sapphire. In that case, symmetric diffraction cannot provide information on the microstructure, as interreticular distance \(d_{135}^{\text{NbN}}\) is too small to observe the corresponding reciprocal lattice point (RLP). For this reason, we have chosen an asymmetric diffraction line. We have investigated the \((3\overline{1}0)\) plane of NbN (Figure 4), by first aligning the R-plane of sapphire and locate its \([1\overline{0}\overline{1}1]\) direction (taken as a reference for \(\varphi\)) by finding the \([3\overline{0}312]\) diffraction peak. We expect the (004) and (133) asymmetrical diffraction peaks of NbN to lie in this \((3\overline{1}0)\) plane. However, the sample used was very thin (6 nm), so that only the (004) NbN RLP could be measured (Figure 4), at the following position (\(\varphi=-40.2°; \omega=12.2°; 2\theta=89.2°\)). The \(c=4.41\) Å axis parameter derived from the 2\(\theta\) measurement is in good agreement with the literature value. The RLP is \(\varphi\) shifted of about 2.5° from the RLP position calculated from the epitaxial relationship. \(\varphi\)-scan (not shown) performed at \(\omega=12.2°; 2\theta=89.2°\) indicates a diffraction peak at \(\varphi=40.2°\), hence symmetrical to the 004 diffraction peak with respect to the \(\varphi=0°\) position. These observations are consistent with information provided by pole figures (Figure 3): the NbN film is twinned with respect to the \([1\overline{0}\overline{1}1]\) Al2O3 direction, and \([135]\) NbN planes are tilted of about 2° with respect to the sapphire R planes. We check that both twin variants have a similar diffracted intensity, and hence are of the same relative importance.

Closer examination of the distribution of scattered intensity around RLPs is usually referred to as mosaic structure study. Indeed, because of high lattice mismatch, heteroepitaxial NbN films on sapphire exhibit high dislocation density and their structure can be modeled by the juxtaposition of mosaic blocks [15]. Those blocks have a certain lateral and vertical dimension corresponding to a coherent scattering. They can also be disoriented which leads to the so called mosaic tilt (out of plane rotation) or twist (in plane rotation). All these parameters may in principle be measured from RLP.
shape analysis. The latter shows that the mosaicity is dominated by mosaic tilt, estimated to 1.8° by measurement of the full width at half maximum (FWHM) of the (004) RLP rocking curves. The mosaic twist can be estimated by ϕ-scans to several degrees. A more precise determination of those parameters and a measurement of coherence lengths require detailed investigation, which is beyond the scope this article. However, mosaic tilt and twist is one order of magnitude higher than, e.g., those observed in heteroepitaxial GaN [15]. This may result from the stronger lattice mismatch (of the order of 8% in NbN/R-Al2O3), and also from the more fundamental non stoechiometric character of cubic NbN.

5. Conclusion
We have shown that growth of NbN thin films on M with, e.g. Tc=13.3 K and ρ_{20K} = 110 μΩ.cm for a 4.4 nm thick film grown on a 3 inch wafer, yields better (superconducting) transport properties than growth on R-Al2O3. The quality of the superconducting films on M-plane sapphire is comparable to those grown on MgO. This observation has been correlated to the films microstructure. The twinning of the NbN/R-Al2O3 appears as a key factor for the electrical performances degradation, when compared to untwinned NbN/M-Al2O3. A closer examination of Bragg peak shape exhibits a very high mosaicity, dominated by high mosaic tilt and twist. We will analyze the impact of untwined NbN layers on SSPDs performances.

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References
[1] Gol’tsman G N, Okunev O, Chulkova G, Lipatov A, Semenov A, Smirnov K, Voronov B, Dzardanov A, Williams A, Sobolewski R 2001 Appl. Phys. Lett. 79 705
[2] Rosfjord K M et al. 2006 Opt. Expr. 14(2) 527
[3] A.J. Kerman, et al. 2006 Appl. Phys. Lett. 88 111116
[4] Wang Z, Kawakami A, Uzawa Y, Komiyama B 1996 J. Appl. Phys. 79 7837
[5] “MBE” growth of superconducting materials, Braginski A I and Talvacchio J, in Superconducting Devices, Ruggiero S T, Rudman D A Boston, Academic Press 1990
[6] Tonouchi M, Sakaguchi Y, Kobayashi T 1987 J. Appl. Phys. 62 961
[7] Gao J R, Hajenius M, Tichelaar F D, Klapwijk T M, Voronov B, Grishin E, Gol’tsman G N, Zorman C A, Mehregany M 2007 Appl. Phys. Lett. 91 062504
[8] Larrey V., Villegier J C, Salez M, Miletto-Granizio F, Karpov A 1999 IEEE Trans. Appl. Supercond. 9 3216
[9] Miki S, Fujiwara M, Sasaki M, Wang Z 2007 IEEE Trans. Appl. Supercond. 17 285
[10] Villegier J C, Hadacek N, Monso S, Delaet B, Roussy A, Febvre P, Lamura G, Laval J Y 2001 IEEE Trans. Appl. Supercond. 11 68
[11] Villegier J C et al, to be published
[12] Paratt L G 1954 Phys. Rev. 95 359
[13] Wildes A R, Mayer J, Theis-Bröhl K 2001 Thin Solids Films 401 7
[14] Espiau de Lamaestre R, Odier Ph, Villegier J C to be published in Appl. Phys. Lett.
[15] see e.g. Cherchia R, Böttcher T, Heinke H, Einfeldt S, Figge S, Hommel D 2003 J. Appl. Phys. 93 8918