Ultra-thin NbN films on Si: crystalline and superconducting properties

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Abstract. We present results on superconducting and crystalline properties of NbN films with a thickness smaller than 10 nm. The films were deposited using reactive magnetron sputtering on heated silicon substrates. Zero resistance critical temperatures of about 9 K have been measured for films with a thickness of about 5 nm and reaches values ≈12 K for 10 nm thick films. A value of the superconducting coherence length of about 4 nm was estimated from the measurements of the second critical magnetic field. High-resolution transmission electron microscopy accompanied with electron-spectroscopy techniques was used to analyze the structure, thickness, and film-substrate interface of fabricated films. The interrelations between fabrication conditions, superconducting and crystalline properties of NbN films on Si substrates are presented and discussed.

1. Introduction

Thin NbN films deposited on silicon substrates are widely used for fabrication of hot-electron bolometer (HEB) mixers. These devices are low noise heterodyne receivers of electro-magnetic radiation demonstrating performances suitable for operation in the THz spectral range [1]. The ultimate value of the intermediate frequency (IF) bandwidth of HEB mixers is limited by inelastic electron-phonon scattering and amounts to ≈10 GHz. However, the experimentally demonstrated values of IF bandwidth are about 3–4 GHz [2, 3]. The main reason of this reduced bandwidth is a less than optimum cooling of the phonon subsystem in the films. This process is supported by escape of non-equilibrium phonons from film to substrate and characterized by the phonon escape time $\tau_{\text{es}}$. Since $\tau_{\text{es}}$ is directly proportional to the thickness $d$ of a film a lot of effort is put into the fabrication of films with thicknesses as small as possible. Superconducting and normal state properties of NbN films with a thickness comparable to the superconducting coherence length $\xi$ become strongly dependent on
d [4]. Thinner films are characterized by larger resistivity and lower critical temperature. Temporary stability of ultra-thin films is worse in comparison to thicker films and therefore limits potentials of devices made from these films. This makes each step of the reduction of film thickness more and more complicated when only few unit cells of superconducting material appear on the surface of a substrate after deposition.

The phonon transport between film and substrate is also determined by phonon transparency of the film-substrate interface [5]. Ideally the transparency of interface is determined only by matching of phonon spectra in film and substrate. Theoretical estimations of transparency and its comparison with experimental results are complicated since in reality a surface of substrate and adjacent layer of deposited film differ from perfect, atomically flat surfaces. Moreover, during deposition the substrate surface can be additionally modified, sometimes in an unpredictable manner. The structural properties of a film nucleation layer, which is in direct contact with a substrate, differ from the structure of the following layers of the film.

Information about the microscopic structure of the film and interfaces required for optimization and development of a deposition process of ultra-thin films can be obtained by transmission electron microscopy (TEM) accompanied by element analysis. In this work we present results on a study of the crystalline structure and elemental composition of thin NbN films deposited on Si substrate together with an analysis of the thickness dependence of the critical temperature of NbN films.

2. Thin-film technology and TEM sample preparation

The NbN films were deposited on 10×10 mm² both-side polished single-crystalline Si substrates of (100) orientation fabricated by floating-zone method. Base pressure in the deposition chamber created by a turbomolecular pump was about 3*10⁻⁷ mbar at ambient temperature. For deposition of NbN films the substrates were directly placed on the surface of a heater without any thermo-conducting glue. The temperature of the heater was kept at 825 °C during deposition. The pressure in the chamber raised with increase of the heater temperature and reached a value of about 10⁻⁶ mbar. Before deposition a two inch diameter Nb target was cleaned by sputtering of the target surface layer in pure Ar atmosphere at a pressure \( P_{\text{Ar}} = 3*10^{-3} \) mbar. A flow of nitrogen gas was then added resulting in a \( P_{\text{N}_2} = 6*10^{-4} \) mbar. After stabilization of a discharge voltage the shutter was opened to deposit a NbN film onto the substrate. We varied deposition times from 18 to 40 s. After cooling of the heater to ambient temperature the substrate with deposited film was taken out.

The determination of the NbN film thickness on Si is a challenge having no easy solution. Deposition on heated substrates excludes the possibility to use lift-off techniques for patterning. Other patterning methods like ion milling or reactive ion etching are not applicable since the etching rate of Si is much larger than the etching rate of the NbN film. Non-destructive methods like ellipsometry and Rutherford backscattering require optical or material parameters to estimate the thickness of the analyzed film. The situation is even more complicated since the properties of NbN are strongly dependent on its stoichiometry and subsequently on fabrication conditions. An average value of the deposition rate of NbN film \( \approx 0.25 \) nm/s was estimated from the thickness of the 20 s deposited NbN film determined from TEM analysis (see below).

The HEB mixer is a superconducting micro-bridge made from NbN film and embedded into an antenna structure typically made from thick gold layer by lift-off technique [3]. Deposition of gold is preceded by deposition of a buffer layer of some getter material. Therefore we deposited onto the ultra-thin NbN film a thin layer \( \approx 20 \) nm of pure Nb. This deposition was made by magnetron sputtering at room temperature after an initial characterization of the thin NbN film.

For TEM inspection cross-section specimens were prepared from the original wafer in the usual way, including gluing of two pieces 2 × 5 mm² in size face to face, grinding, polishing and dimpling down to a thickness of some 10 – 20 μm. Finally, electron transparency was obtained by Ar⁺ ion milling.
Figure 1. HRTEM image of an Nb/NbN bi-layer structure on Si substrate. Dashed lines denote approximate location of interfaces.

Figure 2. Electron energy loss spectra across an Nb/NbN bi-layer on Si substrate: Nb, Si, O, and N profiles. Spectra are shifted for better visibility.

3. High-resolution and analytical TEM

Microstructural investigations of the Nb/NbN/Si layer system were performed by transmission electron microscopy using a Philips CM 200 S/T microscope at 200 kV accelerating voltage and an image-corrected FEI TITAN 80-300 at 300 kV. Data on the chemical composition were obtained by electron energy loss spectroscopy (EELS) in combination with scanning TEM (STEM) using an electron probe of about 3 Å in diameter. For EELS a Gatan imaging filter GIF Tridiem was used.

Structural details of the very interface region between substrate and deposited layers are revealed by high-resolution TEM imaging (figure 1). On top of the Si substrate a silicon oxide of about 1.5 nm mean thickness is present. The adjacent NbN layer has a nanocrystalline structure. Owing to this morphology the thickness of the NbN is not homogeneous at the atomic scale, instead it varies between about 4.5 and 5.3 nm. There is no orientation relationship visible of the individual NbN crystallites and the underlying Si substrate. This behavior can be attributed to the native Si oxide layer. The topmost layer, i.e. the Nb one, is also nanocrystalline. In figure 1 only a part of the Nb layer in direct vicinity to the NbN can be seen. Because of the nanostructure of the NbN and Nb layers the interface in between appears rough. From the image contrast the presence of some amorphous material can be assumed. By comparing the perfectly resolved lattice of Si (lattice constant 0.543 nm) with the crystalline structures of NbN and Nb layers on top of it, lattice constants of approximately 0.44 nm and 0.33 nm, respectively, have been found for both films. Owing to the value experimentally obtained for NbN the presence of stoichiometric NbN can be assumed.

The element distribution across the layer system was studied by recording EEL spectra with a 3 Å electron probe along a line of 30 nm extension. For this purpose spectra were taken at 100 points for 2 s at each measuring point in the range from about 70 eV to 570 eV with a dispersion of 0.3 eV/channel. The corresponding line profiles obtained by means of the Si-L23 and Nb-M45 edges are given in figure 2a, whereas those of the N-K and O-K ones can be seen in figure 2b. The interface region between Nb and NbN contains oxygen. The niobium oxide in this layer results from contamination of the NbN surface after exposing the deposited film to air. Nitrogen is also present in the native Si oxide, i.e. in the interfacial region between Si substrate and NbN film. It can be assumed that it was incorporated during the NbN deposition under Ar/N2 atmosphere. Thus there is an overlapping region between NbN film and Si substrate where all four elements (Nb, N, O, Si) have been found. The high substrate temperature is one of several possible reasons leading to the formation...
of this amorphous layer. The inter-diffusion process can also be intensified by discharging effects during deposition.

4. Properties of NbN films

Right after deposition the temperature dependence of the resistance \( R(T) \) of thin NbN films was measured in the temperature range from 4.2 K up to room temperature by standard four-probe technique. The films show negative dependence of \( R(T) \), i.e. increase of resistance with decrease of temperature. At temperatures \( \approx 20 - 30 \text{ K} \) the resistance reaches a maximum, which is a factor of 1.2 - 1.4 larger than the resistance measured at room temperature. Below the maximum the resistance gradually decreases and is followed by the superconducting transition. The width \( \Delta T \) of the transition defined as 10/90 \% of \( R_N \) was \( \approx 1 \text{ K} \) for the thickest films with \( d \approx 10 \text{ nm} \) and broadened to \( \Delta T \approx 2 \text{ K} \) on the thinnest films \( (d < 5 \text{ nm}) \). The thickness dependence of the zero resistance critical temperature measured using a Si-diode temperature sensor with accuracy \( \pm 0.5 \text{ K} \) is shown in figure 3. The \( T_C \) value increases with thickness and does not show a clear saturation at large values of \( d \). The temperature dependence of the second critical magnetic field \( H_{C2}(T) \) has been measured using a 9 T solenoid in the temperature range about 4 K below \( T_C \). The magnetic field was applied perpendicular to the surface of the film. The zero temperature coherence length \( \xi = 4.4 \text{ nm} \) has been estimated from \( dH_{C2}/dT \) value of linear dependence of \( H_{C2} \) near \( T_C \) [6]. Thus the thickness of our films appears to be less than \( 2\xi \), while the thinnest films were only slightly thicker than the coherence length.

5. Discussion

The critical temperature of our NbN film on Si is almost two times lower than \( T_C \approx 17 \text{ K} \) of bulk samples. Reduction of \( T_C \) in thin superconducting films was experimentally observed [7-9] and described in terms of the intrinsic proximity effect theory first suggested by Cooper [10] and recently generalized by Fominov and Feigel'man [11]. In frame of this theory the film is considered as a three-layer NSN structure, where the superconducting interaction is destroyed in a surface layer of the film and in the layer near the interface between film and substrate. As a result the superconductivity of the center part of the film is suppressed and the measured value of \( T_C \) of the whole structure is lower than in bulk samples. According to [11] \( T_C \) of a NSN structure can be estimated from

![Figure 3. Dependence of the zero-resistance critical temperature of NbN films on the film thickness. The circles are experimental points. The solid line is best fit according to equation 1.](image-url)
\[ \ln \frac{T_C^0}{T_C} = -\frac{\tau_N}{\tau_S + \tau_N} \left[ \psi \left( \frac{1}{2} + \frac{\tau_S + \tau_N}{k_B T_C \tau_S \tau_N} \right) - \psi \left( \frac{1}{2} \right) - \ln \left( 1 + \frac{\tau_S + \tau_N}{\tau_S \tau_N \omega_D} \right)^2 \right], \]  

where \( \psi(x) \) denotes the digamma function, \( T_C^0 \) is the critical temperature of a pure superconductor, \( \omega_D \) is the Debye frequency of the superconducting material, \( k_B \) and \( \hbar \) are the Boltzmann and Planck constants. The \( \tau_S \) and \( \tau_N \) quantities for the NSN three-layer system are

\[ \tau_S = \pi \frac{d_S}{V_S} \rho_{\text{int}}, \quad \tau_N = 2\pi \frac{V_N d_N}{V_S^2} \rho_{\text{int}} \]

with \( d_{SN}, V_{SN} \) being the thickness and the Fermi velocity of the S and N layers, correspondingly and \( \rho_{\text{int}} \) is the resistivity of the SN interface.

Superconductivity in surface and interface layers of the NbN films is destroyed due to their oxidation leading to formation of niobium monoxide, which is a normal metal above 1.38 K [12]. Following theoretical approach described in [10, 11] we estimate an effective thickness \( d_N \) of surface and interface layers with destroyed superconductivity for our NbN film assuming that the superconducting interaction inside nano-crystallites is of the same order as in bulk NbN. Calculations were made assuming ideal interface between superconducting and non-superconducting parts of NbN film, i.e. in Cooper’s limit, where \( \rho_{\text{int}} \rightarrow 0 \) (the transparency of the interface approaches unity). We obtained \( d_N \) about 0.6 nm using the Debye temperature \( \Theta_D = 300 \text{ K} \), and the critical temperature of infinitely thick film \( T_C^0 = 15 \text{ K} \) for the best fit of our experimental data. Therefore the effective superconducting thickness of our films are about 1.2 nm smaller than the physical/geometrical one.

The value of \( T_C^0 \) is lower than critical temperature reported for bulk NbN. There are several possible reasons for reduction of the \( T_C^0 \) value. One of them is deviation of composition of deposited material from the optimal one resulting in weakening of superconducting interaction in the film. Nanocrystallite structure of the deposited NbN films can be also considered as a cause of lower \( T_C^0 \). It has been shown in [13, 14] that critical temperature of NbN films with different thickness (up to several hundreds nanometer) is dependent on diameter of grains, which is determined by the film deposition conditions. Nevertheless the \( T_C^0 \) value of NbN films discussed in this paper is higher than the critical temperature of infinitely thick films found for the NbN films we deposited onto substrates kept at room temperature during deposition [4].

Conclusion
We have fabricated NbN films with a thickness \( \approx 5 \text{ nm} \) and critical temperature \( \approx 9 \text{ K} \) deposited onto heated Si substrate using reactive magnetron sputtering. Results of TEM and EELS analyses show that high substrate temperatures during deposition result in the formation of an amorphous layer at the film-substrate interface due to inter-diffusion of elements (Nb, Si, N, O). Proximity effect between this interface layer, the central superconducting part of the NbN film and the surface layer containing niobium oxide suppresses superconductivity in the NbN film. Further improvement of superconductivity and phonon dynamics in ultra-thin NbN films on Si substrate requires optimization of the film deposition process at lower temperatures and a modification of the Si substrate surface before deposition. The situation at the interface between the NbN film and the Nb buffer layer is more delicate. The technique used for modification of the surface of the ultra-thin NbN film before deposition of a buffer layer should not destroy superconductivity in this film. At the same time the contact resistance between these two layers should be minimized.

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