Abstract

In the recent years, RF cavity performance has reached close to the theoretical limit for bulk niobium. Striving for further improvement in RF cavity performance for future accelerator projects has brought a renewed research interest to superconducting materials other than niobium. Higher-$T_c$ superconductors suitable for SRF applications are being investigated in different laboratories, universities and companies around the world. In this contribution I will focus on two of the prospective superconductors, NbN and MgB$_2$, presenting the coating methods and RF properties at low and high fields.

INTRODUCTION

The accelerating gradient of superconducting niobium cavities is fundamentally limited by the magnetic critical field of niobium, which is the superheating critical field of about 200 mT. Although this limit can be circumvented with re-entrant/lowloss cavity shapes, there is a limit on the reentrance dimensions in the multi-cell accelerator cavities. For this reason superconductors with a higher critical temperature, and accordingly a higher thermodynamic critical field, are of interest for the applications in the field of RF superconductivity. Although there are a lot of superconductors with a transition temperature higher than that of niobium (9.2 K), other requirements such as a low normal-conducting resistance and the possibility to be deposited on complex shapes curtail the number. Both NbN and MgB$_2$, being a simple binary compounds with a number of deposition techniques available, are suitable for RF cavity applications due to the metallic behavior and transition temperatures higher than that of niobium. The low-temperature normal-conducting resistance typically measured in this compounds are of the order of a few $\mu$Ω cm, an order of magnitude higher than that of niobium, and the residual resistivity ratios (RRR) are typically only slightly above one. Still, because of a bigger energy gap these compounds theoretically offer an order of magnitude improvement in RF resistance at low temperatures. And recent developments in coating methods made possible NbN and MgB$_2$ films that have the low-temperature normal-conductivity values equal to those of niobium and the RRRs of about 100, making these compounds particularly attractive.

Moreover, Gurevich proposed that the surface breakdown field in SRF cavities can be significantly increased by a multilayer coating, i.e., when niobium is coated with sequential layers of a thin dielectric and a thin superconductor, [1]. According to the theory the benefit of lower critical field enhancement in thin films can be utilized to reduce the field on the niobium substrate, if, or when, the ability to coat a thin film of a good superconductor on top of niobium substrate is developed.

The potential of these superconductors have been long realized and a number of studies have been carried out on both NbN and MgB$_2$; these studies include developments of coating methods as well as RF measurements of coated samples by the host-cavity method, RF stripline measurement, dielectric cavity measurements, etc. It has been shown that both NbN and MgB$_2$ coatings can have resistances lower than that of niobium, so far, however, no cavity, either with NbN or MgB$_2$ coating, has been produced that had a lower resistance in the whole temperature and field ranges that of the best niobium cavities.

A number of reviews on new materials with the emphasis on SRF applications have been given before [2], [3], [4], [5], etc. The purpose of this review is to iterate the necessity of studying materials other that niobium for future application, and, perhaps, to bring attention to recent developments in the coating methods that may produce a high-quality films for SRF applications. In this contribution I will review some of the results that have been obtained for both compounds. Since the results often vary considerably depending on the coating method, and different coatings may be suitable for different applications, results will be collected with respect to the coating method.

NbN FILMS

A number of different phases has been identified for the Nb-N system: $\alpha$-Nb(N) solid solution (bcc), $\beta$-Nb$_2$N (hexagonal), $\gamma$-Nb$_3$N$_{3x}$ (tetragonal), $\delta$-NbN$_{1-x}$ (fcc), $\eta$-NbN (hexagonal), $\delta'$-NbN (hexagonal) and some N-rich phases (Nb$_5$N$_6$, Nb$_7$N$_5$). Of interest for the superconducting RF applications are the $\delta$-phase and $\gamma$-phase, for which the superconducting transition temperatures of 15 - 17.3 K and 12 - 15 K respectively have been measured. In Fig. 1 the phase diagram for Nb-N system around the phases of interest from [6] is presented. Because of possible applications in microelectronics the deposition and superconducting properties of Nb-N system have been extensively studied. Rather than reviewing all the results from all the different coating methods I decided to focus on the techniques that have been already tested for SRF applications, such as sputtering and thermal diffusion, and also on a recently developed promising deposition method, polymer assisted deposition (PAD).
Figure 1: The phase diagram of Nb-N system around the phases of interest for SRF applications, δ-phase and γ-phase, from [6].

**Sputtering**

Sputtering of niobium is typically done in N₂-rich atmosphere with Ar as the sputtering gas. The substrate temperatures vary from the room temperature up to 1000 °C, and it is one of the main parameters that define the growth of the film. The transition temperatures up to 17 K have been produced by the magnetron sputtering, but the films usually have low RRR because of the columnar structured grains with voids and impurities in between.

In [7], microwave measurements of the films prepared by DC magnetron sputtering were reported. The measurements were done at different frequencies by the stripline and host cavity techniques. The transition temperature was reported to be 15.3 K for all films. The film thickness in the stripline measurement was 800 nm. The penetration depth, \( \lambda(0) \), was reported to be 370 ± 30 nm. The surface resistance values were about 300 nΩ at 4.2 K and the frequency of 1.2 GHz (cf. \( R_{Nb} \approx 150 \Omega \)), and was found to follow the f² law for the frequencies from 6 to 60 GHz.

Nigro et al. reported study on the optimization of deposition parameters, [8]. The highest transition temperature, realized for N₂ partial pressure of about 4 - 8 mTorr, was around 17 K. Still, the RRR values reported in this study were around 1 with the normal-conducting resistivity of about 60 - 300 \( \mu \Omega \cdot \text{cm} \) (cf. \( \rho_{Nb} \approx 0.1 \mu \Omega \cdot \text{cm} \)). No RF measurements of NbN films were reported in this study.

The sputtering method is potentially attractive for SRF cavity applications because this method does not require a thick sheet of niobium to produce an accelerating cavity. Instead a niobium nitride film can be deposited onto any substrate such as, e.g., copper, which in the case of superconducting cavities would mean better thermal stability and materials cost savings in the production of a large number of cavities.

**Thermal Diffusion**

Thermal diffusion thin film coating is done by heating a niobium substrate in the N-rich atmosphere. Thermal diffusion produces more uniform films with higher residual resistivity ratios, which however are prone to inclusions of other, non-superconducting phases. The thermal diffusion technique was studied with the particular emphasis on application for SRF technology. In [9], P. Fabbriacatore et al. reported RF measurements of a niobium nitride cavity made by nitridation of a niobium cavity at 1700 K in 20 kPa nitrogen atmosphere for 1.5 hours. A niobium sample treated under the same conditions showed a superconducting transition at 14.3 K. The X-ray diffraction analysis showed the presence of α, β, and γ phases. The surface resistance measurements showed the surface resistance values of 1.15 \( \mu \Omega \) at 4.2 K for 4.587 GHz frequency (cf. \( R_{Nb} \approx 2.5 \mu \Omega \)). The measurements at lower temperatures have shown that the cavity had a high residual resistance of about 0.69 \( \mu \Omega \). Fig. 2.

A study covering several compounds was done by G. Gemme et al., [10]. Among different compounds the RF properties of NbN samples were studied by the host-cavity method. The nitridation was done in 150 mTorr N₂ atmosphere at 1400 °C for 4 hours, followed by the rapid cooldown from about 1280 °C to 950 °C in 3 min. Niobium nitride δ’-phase was observed after such treatment, but it was suggested by the authors that a pure δ-phase may be obtained by reducing the cooldown time to 1 min. The superconducting transition temperature was measured to be (15.63 ± 0.06) K. The quality factor of 7.9 GHz RF cavity with such sample was measured above 9.2 K. From the data nine material parameters of the film were calculated.

**Figure 2:** \( R_s \) vs. T for 4.5 GHz NbN cavity, made by nitridation of a niobium cavity. Note, \( R_s \) of this cavity at 4.2 K, 1.15 \( \mu \Omega \), is lower than that of niobium at this temperature and frequency, \( \approx 2.5 \mu \Omega \). This NbN cavity, however, had a high residual resistance of about 0.69 \( \mu \Omega \). [9].
the calculated parameters the BCS surface resistance at 4.2 K was calculated to be around $1.3 \times 10^{-6}$ and at 1.8 K around $1.3 \times 10^{-10}$ for 7.9 GHz frequency. It should be noted, that the measurements were done above 9.2 K, so no data on the residual resistance for these samples was collected, and also that material parameters were derived from fitting of a single curve with nine parameters.

**Polymer Assisted Deposition**

Recently, niobium nitride films of very high quality have been reported by G. Zou et al. [11]. An aqueous solution of niobium ion bound to polymer was spin coated on the sapphire, and then annealed at 900 °C for 5 hours in gaseous ammonium. The superconducting transition was observed at about 14 K. The relatively low transition temperature and temperature suggest that the $\gamma$-phase was formed. The low-temperature resistance was measured to be 0.4 $\mu\Omega$-cm at 20 K (cf. $\rho_{Nb} \approx 0.1 \mu\Omega$-cm at 10 K), and the RRR was accordingly 98.4, giving these films the highest RRR reached in the niobium nitride films.

Although the RF properties of these films have not been measured yet, the results from the DC measurements are very promising, because they hint to a low BCS resistance because of the low normal-conducting resistance. Also, this method could be directly applied to the cavity shape if the aqueous solution of niobium ion bound to polymer is dipped coated on the cavity surface, and then annealed in N-rich atmosphere.

**MgB$_2$ FILMS**

The phase diagram in Fig. 3 from [12] shows the composition of Mg-B system as a function of the substrate temperature and partial pressure of Mg. The window corresponding to a clean superconducting MgB$_2$ phase is denoted in the 3 as "Gas + MgB$_2". A number of techniques have been developed to grow superconducting MgB$_2$ films: hybrid physical-chemical vapor deposition (HPCVD), molecular beam epitaxy (MBE), reactive evaporation, ultra high vacuum molecular beam epitaxy (UHV-MBE), electron beam evaporation (EBE), ultra high vacuum-electron beam evaporation (UHV-EBE), and pulsed laser deposition (PLD). Again, since our goal is too review MgB$_2$ properties with the emphasis on SRF applications only some of the techniques are presented here, viz. techniques that have been most widely tested in RF regime and are promising for SRF applications.

So far, the best results have been produced by the reactive evaporation technique and by the hybrid physical-chemical vapor deposition.

**Reactive Evaporation**

Reactive evaporation technique was developed by B. H. Moeckly et al., [13], by modifying the existing YBCO deposition system. The system has a pocket heater with a rotating substrate holder. Mg vapor is provided by a thermally heated Mg source in the pocket near the rotating holder. A third of the rotation cycle the holder is also exposed to B vapor, provided by e-beam evaporation of a pure boron source. The boron layer reacts with Mg to form MgB$_2$ when the substrate is inside of the pocket heater, and the cycle repeats itself. Very high quality films of MgB$_2$ have been deposited at the substrate temperature of 550 °C. Th superconducting transition temperatures up to 39 K have been reported, as well as normal-conducting resistivities of about $2 \mu\Omega$-cm (cf. $\rho_{Nb} \approx 0.1 \mu\Omega$-cm at 10 K) and RRR values of more than 4. In Fig. 4 the surface resistance of such MgB$_2$ film measured by the parallel plate and by the stripline techniques is shown. It was found to be of the order of $20 \mu\Omega$ at 10 GHz (cf. $R_{Nb} \approx 70 \mu\Omega$ measured with the same setup), [14].

Recently, 100 nm thick films of MgB$_2$ have been deposited on single-grain niobium samples, [15]. The samples have been tested by the host cavity method in 11.424 GHz cavity, [16]. The films have shown two superconducting transition, one at about 37 K, corresponding to MgB$_2$, and the other at about 9 K, corresponding to Nb transition. The breakdown of superconductivity of the sample was observed at about $\mu_0 H = 40$ mT at 4 K (cf. $\mu_0 H_{breakdown} \approx 120$ mT as measured with the same setup). Preliminary results, however, suggest that the breakdown of superconductivity was in the niobium substrate. More extensive studies are planned to understand the cause of the premature breakdown and to improve the limiting field.
Figure 4: \( R_s \) vs. \( T \) scaled to 10 GHz for MgB\(_2\) films, deposited by the reactive evaporation technique, [13], on sapphire (circles), a YBCO film on LAO (triangles), and for Nb thin films (squares). Filled symbols indicate the parallel plate measurements with external losses subtracted, and open symbols indicate stripline resonator measurements including external losses, [14]. Note that at 4 K the resistance of MgB\(_2\) film is about 5 times lower than that of Nb.

**Hybrid Physical-Chemical Vapor Deposition**

The best quality MgB\(_2\) films have been produced so far by the hybrid physical-chemical vapor deposition technique, [17]. The superconducting transition temperatures of more than 40 K and the low temperature resistivity of 0.1 \( \mu \Omega \) cm at 40 K have been reported, [18]. These films reached the record RRR for MgB\(_2\) films of almost 80. In this method, the Mg is provided by thermally evaporating bulk Mg pieces (physical vapor deposition) and the B is provided by the precursor gas, \( \text{B}_2\text{H}_6 \), (chemical vapor deposition) mixed with \( \text{H}_2 \) to suppress oxidation of Mg. The method provides a high Mg vapor pressure that satisfies the thermodynamic phase stability condition at the temperature used for the deposition, as the results the films of the highest quality are obtained.

**Annealing of B Films in Mg Vapor**

One of the earliest methods for creating an MgB\(_2\) film was annealing of B film in magnesium atmosphere, [19]. This method has been proposed as the most suitable to produce a high quality coating on the complex shapes like SRF cavities, [21].

In this technique boron is deposited on the substrate wall by decomposition of B-containing gaseous mixtures such as, e.g., \( \text{H}_2 + \text{B}_2\text{H}_6 \). After the formation of boron layer, the heated substrate could be exposed to Mg vapor to form the MgB\(_2\) layer. Recently, films from 1 to 10 \( \mu \text{m} \) thicknesses were deposited with this method. The films had RRR of about 10 and the transition temperatures of 40 K, [20]. The low temperature resistivity of the films was measured to be less than 2 \( \mu \Omega \) cm, which is comparable to that achieved with the reactive evaporation method.

**CONCLUDING REMARKS**

In the recent years, RF cavity performance has reached close to the theoretical limit for the bulk niobium. Striving for further improvement in RF cavity performance for future accelerator projects has brought a renewed research interest to superconducting materials other than niobium. NbN and MgB\(_2\) are two of the prospective superconductors, which can significantly increase the performance of superconducting cavities. In this contribution the RF results for some of the deposition methods have been reviewed. Since different methods have different advantages, it is impossible to choose one coating method that would be the most suitable for coating an SRF cavity. However, considering the work done so far the best results for NbN cavities were achieved with the thermal diffusion method, and for MgB\(_2\) coatings, for which no MgB\(_2\) coated niobium cavity have been produced so far, annealing of B films in Mg vapor seems to be the most promising.

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