RAPID COMMUNICATION

High quality superconducting niobium films produced by an ultra-high vacuum cathodic arc

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Abstract
The vacuum arc is a well-known technique for producing coatings with enhanced adhesion and film density. Many cathodic arc deposition systems are actually in use in industry and research. They all work under (high) vacuum conditions in which water vapour pressure is an important source of film contamination, especially in the pulsed arc mode of operation. Here we present a cathodic arc system working under ultra-high vacuum conditions (UHVCA). UHVCA has been used to produce ultra-pure niobium films with excellent structural and electrical properties at a deposition temperature lower than 100 °C. The UHVCA technique therefore opens up new perspectives for all applications requiring pure films and low deposition temperatures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The vacuum arc is one of the oldest techniques used for depositing thin films. Its main advantages over other techniques are the ionized state of the evaporated material and the high ion energy [1], allowing deposition of films with enhanced adhesion and higher density [2]. In recent years important progress has been made in understanding the role of the cathode cohesive energy in the interplay between arc voltage, erosion rate, kinetic ion energy and applied magnetic field [1, 3]; the role of potential and kinetic energy in atomic scale heating has been pointed out as well [4].

The problem of macroparticle production on the cathode surface, affecting the arc sources, has been overcome, thanks to the improvement in magnetic filtering, to the point that defect-free films can be deposited [5]. The way to new applications where a smooth surface is needed has thus been opened.

To increase the ionization state of the plasma ions and to reduce the thermal load on cathode and substrate, several groups developed and used the pulsed vacuum arc technique [6], which also reduces macroparticle emission. By varying the arc discharge duty cycle and applying a pulsed bias to the substrate, the film properties can be further optimized. As an example of the pulsed technique potential, uniform films have been deposited on a substrate with a series of 130 nm wide and ~1 µm deep parallel trenches [7].

On the other hand, problems have been reported both in the pulsed and in the DC modes of operation [8] of conventional systems operating in high vacuum (~10\textsuperscript{-5} Pa), such as incorporation of oxygen and hydrogen in films [9]. The problem is believed to originate from the water vapour layer that forms on the cathode surface in between arc pulses because of the residual water vapour present in the chamber, and it has limited the use of cathodic arc deposition to applications where purity was not a fundamental issue. The problem can be solved by lowering the pressure to UHV standards, thus opening the way towards applications requiring ultra-pure metallic films.
We present here the first UHV cathodic arc (UHVCA) system designed mainly in view of application to niobium coating of superconducting RF cavities for particle accelerators [10]. It is in fact expected that Nb arc-coated Cu cavities would allow reaching useful accelerating fields higher than the present $\sim 15 \text{ MV m}^{-1}$ of cylindrical magnetron sputtered ones.

2. Experimental details

A schematic drawing of the systems is shown in figure 1. It is pumped down by an oil-free pumping system consisting of a membrane pump on the foreline of a turbo molecular drag pump, and reaches a base pressure of $\sim 1 \times 10^{-8} \text{ Pa}$ after a 12 h bake-out at 150°C. Ignition of the arc at such a low pressure is not only more critical than for a standard arc device, but the triggering system must also be absolutely ‘clean’ so as not to contaminate the plasma. A common triggering method that uses high voltage discharge across the surface of an insulator had to be discarded because traces of elements evaporated from the insulator were found in the films, particularly when several ignitions were needed during a single deposition. After testing several other methods [11] a laser triggering system has been finally adopted. A compact 50 mJ Nd–YAG laser focused on the cathode is sufficient to most reliably ignite the arc under the cleanest possible conditions$^5$. To prevent contamination due to memory effects when the same system is used to deposit different materials [13] we have only used high purity niobium cathodes.

Vacuum conditions before and during the discharge are checked using a residual gas analyser (RGA). Immediately after the arc is started, outgassing of light elements (mainly H$_2$, CO, hydrocarbides and water) is observed, but after $\sim 1$ min of operation the partial pressure of all outgassed species other than hydrogen, directly coming from the Nb cathode, falls to below $\sim 10^{-7} \text{ Pa}$. The total pressure during DC operation is typically in the $10^{-5} \text{ Pa}$ range, 99% of it being due to hydrogen (see figure 2). As soon as the arc extinguishes the hydrogen pressure drops one order of magnitude, reaching its equilibrium pressure in presence of a fresh oxide-free Nb surface, and then starts slowly decreasing, pumped by the 200 l s$^{-1}$ turbomolecular pump.

Niobium films have been deposited on both copper and sapphire substrates. Samples were placed on an electrically insulated sample holder, at about 50 cm from the cathode surface. A constant 40 V bias was applied to holder so as to deflect electrons and collect only the multiply charged, $> 100 \text{ eV}$ kinetic energy Nb ions [1]. The thermal load on the sample was thus much reduced, and a thermocouple placed on the sample holder indicated that the substrate temperature was kept below 100°C during the deposition. The average kinetic energy of the Nb atoms, reaching the substrate with an average charge of +3, is estimated to be $\approx 250 \text{ eV}$, a value large enough to produce some sputtering from the growing film. The lowest arc current for stable operation was about 60 A, and its maximum value, limited by our cooling power, was 160 A in the DC mode.

3. Experimental results and discussion

Samples were produced at several arc current values and their electronic and structural properties analysed. We checked the purity of our films with some quantitative techniques (mainly Auger and XPS) using an argon ion gun to measure the depth profile. After removal of the first oxidized layer, the contaminants were below the detection limits of these

$^5$ More details on the system can be found in [12].
techniques (0.1% at the best). Inductive measurements of the superconducting critical temperature \( T_c \) (9.26 K for pure bulk Nb), very sensitive to impurity and stresses, were carried out in order to have an indication of the film quality. It is for instance known that very small amounts of oxygen in the film can lower \( T_c \), while compressive stresses can raise it up to 9.6 K [14].

The superconducting critical temperature of the niobium films were measured inductively using a single coil placed on the sample surface. A small sinusoidal current passes through the coil, while a lock-in amplifier records the change in the third harmonic amplitude generated during the transition between the normal and the superconducting state in a similar way to that reported in [15]. We used a frequency of 10 kHz and a low current amplitude (of the order of few microamperes) in the primary coil and we checked that the measured critical temperature and transition width do not depend on the current amplitude in the range of current used.

Typical results are shown in figure 3 for six samples. Differences in \( T_c \) compared to the bulk value (bulk \( T_c = 9.26 \) K) are small and can be in part due to small temperature differences between the thermometer and the samples. No dependences on either film thickness, in the 0.1–2 \( \mu \)m range, or arc current were found, all samples being of high quality. The sharp transition widths (<0.02 K), close to that of bulk Nb, are strong indicators of uniform and clean films. The absolute \( T_c \) values indicate that stresses in the films are lower than in the magnetron sputtering case.

![Figure 3. Inductive \( T_c \) measurement for six typical niobium samples produced by UHVCA. The film thickness ranges from 100 nm to 2 \( \mu \)m. The sharp transition width (<0.02 K) is similar to that of the bulk, and gives a strong indication of uniform and clean films. The absolute \( T_c \) values indicate that stresses in the films are lower than in the magnetron sputtering case.](image)

Figure 4. (a) SEM image of a niobium film surface showing the presence of macroparticles, molten niobium drops originating from the niobium cathode. The largest droplets in this picture are 6 \( \mu \)m in diameter. (b) Inductive \( T_c \) measurements for two Nb samples with macroparticles covering a large fraction of the surface. For each sample two transitions are visible, the first due to the film and the second due to macroparticles. In both cases the transition widths are about 0.01 K for both film and bulk. Small differences in the macroparticle \( T_c \) are within the instrument reproducibility error (about 0.03 K).

![Figure 4. (a) SEM image of a niobium film surface showing the presence of macroparticles, molten niobium drops originating from the niobium cathode. The largest droplets in this picture are 6 \( \mu \)m in diameter. (b) Inductive \( T_c \) measurements for two Nb samples with macroparticles covering a large fraction of the surface. For each sample two transitions are visible, the first due to the film and the second due to macroparticles. In both cases the transition widths are about 0.01 K for both film and bulk. Small differences in the macroparticle \( T_c \) are within the instrument reproducibility error (about 0.03 K).](image)

Another parameter very sensitive to impurity is the residual resistivity ratio (RRR), defined as the room temperature resistivity divided by that at 10 K: the higher the RRR, the higher the purity. Typical RRR values of Nb films deposited by sputtering on room-temperature substrates range from 2 to 10, while bulk Nb with RRR in the 40–500 range is commercially available. RRR values measured on our Nb films samples, deposited on sapphire at room temperature, range from 20 to 50, while heating the substrate at 150 \( \degree \)C resulted in niobium films with RRR around 80. RRR values up to 40 can also be obtained by magnetron sputtering in UHV systems but only at substrate temperatures higher than 200 \( \degree \)C, not compatible with all applications (for example, copper substrate is annealed and its mechanical properties degraded; in multilayers deposition diffusion in between layers may occur).

We believe that such a high value of RRR could be obtained in our films thanks to the absence of noble gas to sustain the discharge (always present and a major contaminant in films

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6 Details of macroparticle distributions and filtering are reported elsewhere [12].
deposited by sputtering) and to the atomic-scale heating due to
the kinetic and potential energy of the niobium ions reaching
the film’s surface, resulting in a local temperature higher than
average temperature reached by the substrate and recorded by
the thermocouple.

4. Conclusions

We have produced very high quality superconducting Nb
film samples at room temperature in what we believe is
the first cathodic arc system working in ultra-high vacuum.
The UHVCA system has shown excellent reproducibility and
reliability also thanks to laser triggering. It is ultra-clean,
and after \( \sim 1 \) min conditioning the partial pressures of all
outgassed species other than hydrogen fall to below \( \sim 10^{-7} \) Pa.
The total pressure during arc operation is in the \( 10^{-5} \) Pa
range, 99% of it being due to hydrogen outgassed from
the niobium cathode. The UHVCA system opens the way
towards applications requiring pure superconducting films,
in particular on substrates that cannot be heated at high
 Temperatures. The ionized state of the evaporated material and
the high energy of the ions reaching the substrate make this
technique suitable for reactive deposition of superconducting
compounds like nitrides, carbides and magnesium diboride.

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