Rare gas trapping in sputtered Nb films

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Abstract

Energetic neutrals reflected from the cathode may be substitutionally trapped in films produced by sputtering. Since the recoil energy is larger for light ions bombarding heavy element cathodes, niobium films obtained using argon as discharge gas are expected to contain an appreciable amount of this gas. This effect should be strongly reduced by replacing argon with a heavier gas such as krypton or xenon.

Nb films have been produced using Ar, Kr, Xe and then analysed for rare gas content by thermal extraction. The Residual Resistivity Ratios (RRR) have also been measured.

The gas concentrations were found to vary from the 10^3 ppm range for Ar down to the ppm level for Kr and Xe.

The RRR values were only marginally affected by the change of discharge gas at low discharge voltage (400 V), while at higher voltages (600 V - 700 V) an important difference has been observed.

1. Introduction

Niobium sputter-coated copper RF cavities provide an interesting alternative to the traditional solution based on forming and welding bulk niobium sheets [1]. Thanks to their higher thermal stability, lower cost, higher Q_0 value and insensitivity to trapped earth magnetic field [2] Nb-coated cavities have been adopted at CERN for the energy upgrade of the Large Electron Positron collider (LEP) [3].

Together with these advantages, Nb-coated cavities present however a large Q_0 degradation with increasing accelerating field, a fact which has not been explained to date. Equally unclear are the reasons of the relatively low Residual Resistivity Ratio (RRR) of the Nb films (about 20), compared to the much higher RRR of the Nb sputtering cathode (150 to 300).

The small crystal grain size of the Nb films (about 80 nm, i.e. three orders of magnitude lower than for bulk Nb), the high density of crystallographic defects, impurities present at the Nb-Cu interface or originating during the coating process are all possible causes of these two effects.

Among the impurities which may be trapped in the film during the sputter process a prominent one is the discharge gas, namely argon. Experimental evidence and theoretical arguments [4-7] suggest that discharge gas atoms may be trapped in the film whenever a cathode of atomic mass larger than that of the gas is employed. In this case, discharge gas atoms resulting from neutralisation of energetic ions before cathode collision may be reflected with high energy and get substitutionally incorporated in the growing film. For the simplest case of a two-body interaction between a gas atom of mass M and energy E and a target atom of mass m initially at rest, and for elastic scattering at 90° with respect to the incidence direction (the most typical situation for the case of the considered cylindrical magnetron sputtering configuration), energy and momentum conservation gives the following expression for the reflected atom energy E':

$$E'/E = (M - m) / (M + m) \qquad (1)$$

For the case of a stationary niobium atom, having $m = 93$, and different incident inert gas atoms, eq. (1) provides the E'/E ratios given in Table I.

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Since trapping is only possible for highly energetic neutrals, niobium sputtering with krypton and xenon, instead of argon, should lead to a much lower content of discharge gas in the deposited film.

Inert gas	Atomic mass	*E'/E*
helium	4	0.92
neon	20	0.65
argon	40	0.40
krypton	84	0.05
xenon	131	reflection impossible

Table I: Ratio of reflected to initial energy for different rare gases bombarding a Nb cathode (for scattering at 90° with respect to incidence direction).

2. Experimental facilities and procedures

2.1 Sputtering

Samples of niobium films, deposited on quartz and copper substrates using Ar, Kr and Xe as discharge gases, were produced in a cylindrical magnetron system designed for the coating of single cell 500 MHz accelerating cavities [8]. Three rotatable sample-holders were mounted on different flanges added for this specific purpose to a stainless steel cavity, allowing up to 15 samples to be produced under different conditions within the same coating process.

The pumping of the system is achieved by a 170 l/s turbomolecular pumping station, and after a 24 hours bake-out at 200°C an ultimate pressure in the low 10^{-9} Torr range is reached. The cavity and the sample-holders are heated at 200°C prior to sputtering, and an automatically operated system of fans prevents this temperature from being exceeded during coating. The gas composition inside the system can be monitored by means of a differentially pumped quadrupole mass spectrometer.

The samples were produced at discharge voltages ranging from 400 V to 700 V, with a current of about 7.5 A and a sputtering duration varying between 40 and 50 minutes, so as to obtain a film thickness of the order of 1.5 µm, as for the LEP cavities.

In the case of argon, evidence of the existence of a pumping action during sputtering is given by the steep pressure decay when operating the discharge in static conditions. In order to keep the pressure constant during the process, the discharge gas has instead to be continuously injected, with the turbomolecular pump valved off. The discharge pumping throughput is then obtained from the rate of pressure rise when the discharge has been switched off and gas injection maintained. To improve discharge stability all the samples were actually produced keeping the turbomolecular pump valve open. Even in this case, the discharge pumping can be measured from the instantaneous pressure increase occurring when the discharge is stopped.

2.2 Thermal extraction system

The amount of discharge gas atoms present in the samples was measured using an UHV system equipped with a small crucible which may be heated up to 1500°C. The system is equipped with total and partial pressure measuring facilities which allow an estimation of the amount and the species of the gases released while heating.

After dissolving the copper substrate in nitric acid, the niobium film is placed in the crucible, in close contact with a 99.999% nickel sheet. At a temperature of 1170°C (i.e. far below the fusion temperature of niobium, 2468°C) the eutectic alloy $Nb_{40}Ni_{60}$ is formed, which melts and releases all the inert gas atoms present in the film. The rare gas concentration is then calculated as the ratio of the released gas amount to the Nb mass obtained by sample weighing.

3. Results and discussion

3.1 Rare gas incorporation

Assuming a pumping mechanism as described in paragraph 1, one can expect the pumping throughput to be proportional to the discharge current, when the cathode potential is kept constant. Moreover, the trapping probability of the inert gas atoms increases markedly with their kinetic energy [6]. Therefore one can expect a considerably higher discharge gas incorporation when the cathode voltage is increased.

Discharge pumping throughput measurements for argon are shown in Fig. 1. From the data relative to a discharge current of 7.5 A and from the measured sputtering rates, under the assumption that discharge pumping is only due to Ar incorporation into the growing film, an estimate of the average Ar content of the samples can be obtained. In Fig. 2 the values calculated in this way are compared to those provided by thermal extraction measurement.

As shown in Fig. 3, thermal extraction results indicate that Kr and Xe incorporation in niobium films is about two orders of magnitude lower than for Ar.

3.2 Residual Resistivity Ratios

In order to find out how the rare gas incorporation affects the quality of the niobium films, the RRR of the samples deposited on quartz substrates were measured. The results are plotted in Fig. 4. While at 400 V average RRR values slightly below 20 are obtained either with Ar or with Kr, samples produced at higher discharge voltages give strikingly different results according to the discharge gas employed: a RRR improvement up to about 30 is found with Kr and Xe, as opposed to the considerable decrease noticed with Ar.

To fit the variation of RRR as a function of the Ar concentration c_{Ar}, as shown in Fig. 5, one can write from the definition of RRR:

$$RRR = [14.5\ \mu\Omega cm + \rho_{res}] / \rho_{res} \qquad (2)$$

where 14.5 $\mu\Omega$cm is the phononic contribution to the resistivity at room temperature and ρ_{res} is the residual resistivity of the Nb film at 10 K. The latter can in turn be expressed as a linear function of c_{Ar}, obtaining from the fit the following expression:

$$\rho_{res}\ [\mu\Omega cm] = 0.5 + 300\ c_{Ar}\ [\text{at. fraction}] \qquad (3)$$

4. Conclusions

Sputter-coated Nb films incorporate an appreciable amount of Ar, amount which increases when increasing the applied discharge voltage. Ar trapping results in a RRR decrease which was already observed (but at that time not explained) during the optimisation of the coating parameters for LEP cavities, leading to a progressive reduction of the discharge voltage to 400 V, the value adopted for the standard coating recipe [8].

The incorporation of Kr and Xe at 400 V is lower by two orders of magnitude, and remains negligible even at higher voltages. Contrary to Ar, higher RRR values are obtained with Kr and Xe as discharge gases for higher applied voltages, in spite of the fact that the process of optimising the discharge parameters for these gases has not yet been completed.

5. Acknowledgements

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Figures

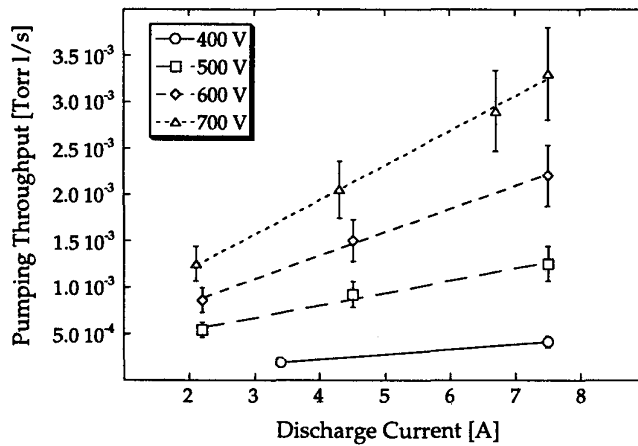

Fig 1. Discharge pumping throughput for argon as a function of the discharge current.

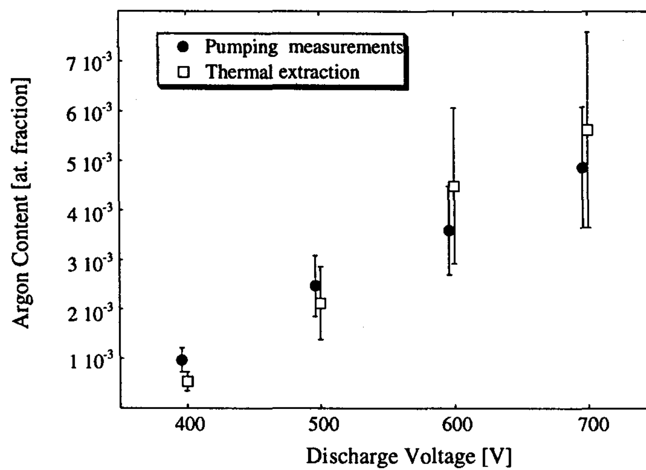

Fig. 2. Argon content as a function of the discharge voltage.

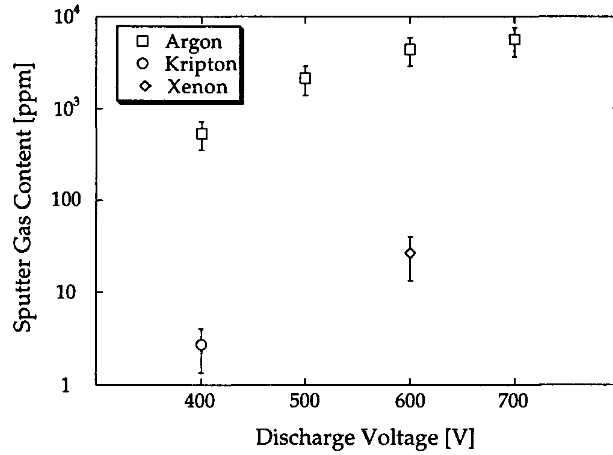

Fig. 3. Ar, Kr, Xe content as a function of the discharge voltage. Thermal extraction measurements.

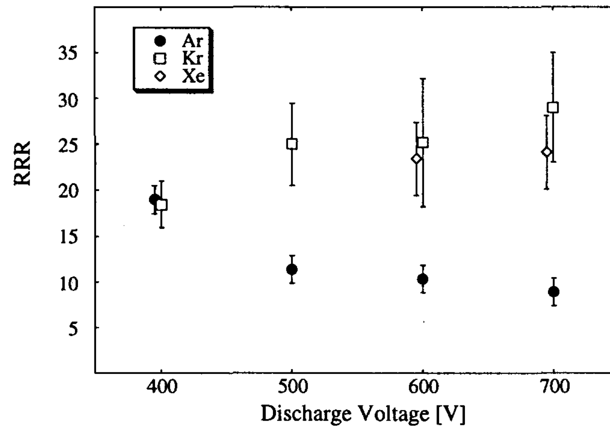

Fig. 4. Variation of the Nb film RRR as a function of the discharge voltage for Ar, Kr, Xe.

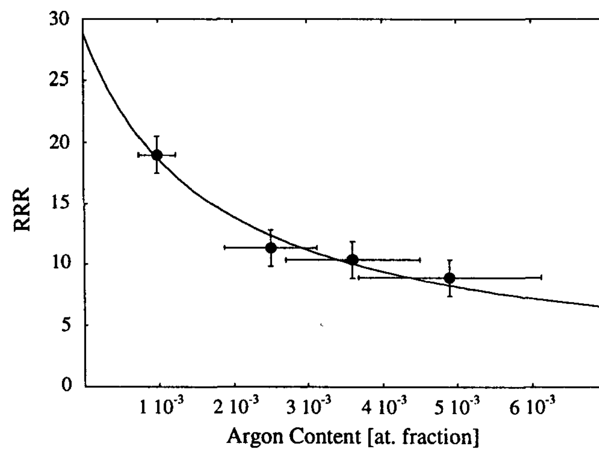

Fig. 5. RRR of the Nb films as a function of the Ar content.