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Liquid nitrogen to room temperature thermometry using niobium nitride thin films

Olivier Bourgeois,* Emmanuel André, Cristina Macovei, and Jacques Chaussy
Institut Néel, CNRS-UJF, 25 avenue des Martyrs, 38042 Grenoble, France

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Niobium nitride thin film thermometry has been developed for the temperature range of 70K to 300K. The deposition parameters have been optimized in order to get the best performances, i.e. the highest temperature coefficient of resistance (TCR), up to 300K. The TCR is found to be largely higher than 1% as the temperature is lowered from 300K, up to 6% at 77K. These significant performances are compared to the one of regular platinum thermometer as well as to other resistive thermometer: semiconductor type or amorphous metal to insulator transition materials. It is discussed how the properties of the NbN thin films could be due to a high temperature Mott transition.

Materials exhibiting metal to insulator transition have been already widely used as resistive thermometer at low temperature [1, 2] and over larger temperature ranges [3]. At low temperature, the interesting properties of niobium nitride (NbN) as well as amorphous Nb-Si have been extensively used to build highly sensitive thin film resistive thermometers due to the significant increase of resistance as the temperature is lowered [2, 3, 4]. There is nowadays an increasing need for such highly sensitive thermometers for measurement closer to the room temperature, especially in calorimetry for applications in nanomagnetism [5], biophysics [6, 7] or infra-red bolometry [8] where specific minute thermal or thermodynamic signatures are being explored.

We report here an original work exploring the performances for thermometry of highly nitrogen doped niobium thin films up to room temperature. The films studied here show characteristics around one order of magnitude better than regular metallic resistive thermometer like platinum thin film in terms of temperature coefficient. These performances are comparable in magnitude to what has been obtained in amorphous Nb-Si [3] or semiconducting like systems as amorphous YBaCuO thin films [8]. By increasing the nitrogen doping we are able to push the metal to insulator transition to much higher temperature than before. The insulating nature of these nitrogen doped niobium materials arises already at room temperature with reasonable thermometer impedance allowing the electrical measurement with a regular low noise measurement chain. Moreover, the deposition process allows the integration of such thin films into any micro or nanofabricated devices.

The NbN thin films were all prepared following the same technique. The films are deposited by reactive sputtering using a pulsed power supply magnetron on a 3.5N purity Nb target in a mixture of nitrogen and argon gases. The base pressure is about 10^{-7} mbar and during the deposition the pressure in the chamber is regulated at 2×10^{-2} mbar. The composition of the gas mixture is controlled by two mass flow debimeter. The proportion

of the two different gases is an adjustable parameter used to control the level of nitrogen doping in the film. The exact proportion of argon and nitrogen in the plasma is also controlled via a mass spectrometer connected to the sputtering chamber. The mass spectrometer also works at low pressure to check the possible existence of impurities like organic materials, oxygen and the presence of water; their presence has been evaluated to be less than 10 ppm. The sample holder is maintained at room temperature using circulating water avoiding any overheating of the thin film during the deposition procedure. The plasma is created by a pulsed power supply with a working frequency tuned between 0 and 350 kHz, the higher the frequency the higher the nitrogen doping in the film. The typical thickness of the films measured with a profiler is about 100nm. The thin films are deposited on sapphire substrate on the voltage and current electrodes as it is depicted in the inset of the Fig. 1.

After the deposition, the films are annealed under vacuum at 150°C for 2 hours. This is a crucial step in the process to stabilize the electrical properties of the thermometer. It prevents the transducer from spurious aging processes and improve its intrinsic temperature coefficient; this has been also reported by other authors [4, 9]. Four different samples are presented in this study, three (sample # 1, 2 and 3) adapted to high temperature measurement and one, sample #4, used as a reference sample. The reference sample is also a NbN thin film having a lower nitrogen doping; this kind of thermometer are regularly used for low temperature calorimetric measurements [10]. Rutherford backscattering (RBS) analysis giving the atomic ratio of nitrogen and niobium is used as a posteriori control of the composition of the films. All the deposition parameters are summarized in the Table I; it is worth noticing that as it will be shown in the following the electrical properties of the films are very sensitive to the atomic proportion of nitrogen and niobium: $x=N/Nb$.

The electrical characterizations are performed using the four probe measurement technique: two leads used to applied the current and two leads for the measurement of the voltage. The thin film thermometer is rectangular but the surface between the two voltage leads where the current density is uniform is a square of 1mm by

*olivier.bourgeois@grenoble.cnrs.fr

TABLE I: Sputtering deposition parameters of the different NbN samples. τ_{Ar} and τ_{N_2} represent the gas (Ar, N) flow in the plasma in sccm (standard cubic centimeter per minute), f the excitation frequency of the plasma in kHz, $x=N/Nb$ the composition of the film measured by RBS (see text) and t the deposition time in minute. The sample # 4 is considered as a reference sample.

| samples | τ_{Ar} | τ_{N_2} | f | x | t |
|-----------|-------------|--------------|-----|------|-----|
| #1 | 1 | 30 | 350 | 1.65 | 10 |
| #2 | 1 | 30 | 350 | 1.65 | 10 |
| #3 | 4 | 30 | 350 | 1.6 | 10 |
| #4 (ref.) | 4 | 14 | 150 | 1.4 | 5 |

TABLE II: Summary of the resistive behavior of the NbN thin films. The resistance given in the table is the resistance per square in Ohm. The sample # 4 is considered as a reference sample.

| sample | R_{300K} | R_{77K} | ρ (m Ω .cm) | RR | α_{300K} (%) | α_{77K} (%) |
|-----------|------------|-----------|-------------------------|------|---------------------|--------------------|
| #1 | 2678 | 186600 | 26.78 | 70 | 0.9 | 5.3 |
| #2 | 1745 | 61100 | 17.45 | 35 | 0.7 | 3.5 |
| #3 | 643 | 62200 | 6.43 | 96.4 | 0.83 | 5.3 |
| #4 (ref.) | 469 | 750 | 4.69 | 1.6 | 0.1 | 0.27 |

1mm. The measuring current varies from 1nA to 1 μ A; IV characteristic were controlled to be linear in that current range. The typical resistance of the films at room temperature lies between 800 Ohm to few kiloOhm. A specific low noise measurement chain has been used based on lock-in amplifier technique and very low noise preamplifier. The resistances have been measured versus the temperature between 70 to 300 K in a 4He cryostat. The variation of the resistances per square of the four samples is presented in the Fig. 1. We choose to plot the resistance per square (R_{\square}) because it is then easier to adapt the thermometer for different applications depending on the chosen geometry of the device transducer. The resistance per square is the resistance of a thin film having a square surface in the plane of the circulating current. A good criterion for a first characterization of the NbN film is the measurement of the resistive ratio (RR), the ratio between the resistance at 77 K and the resistance at 300K. For a low temperature thermometer that ratio has to be around 3 [1], but in our case in order to get a good thermometer in the temperature range of 70K to 300K the RR has been pushed up to 100. All the electrical characterization data are given in the Table II.

It is clear that all the samples exhibit a significant increase of resistance as the temperature is lowered, except for the reference sample. For some sample the increase represents several order of magnitude; it is correlated to a metal to insulator transition occurring early in temperature as it will be discussed further at the end of the paper.

For application in oscillating temperature calorimetry (or ac calorimetry) the figure of merit we favour is

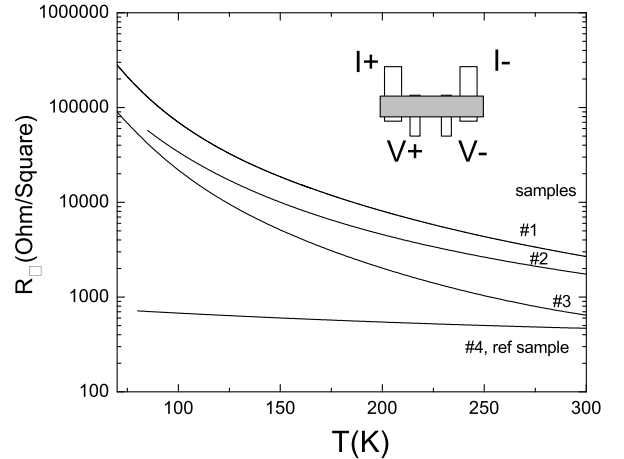


FIG. 1: Resistance per square of the four different samples (measured every mK) (see table I for the details of the deposition parameters) versus the temperature. All samples exhibit an increasing resistance as the temperature is lowered due to a metal to insulator transition. The inset depicts the geometry of the contacts, four electrodes (I+, I-, V+, V-) crossing the thin film.

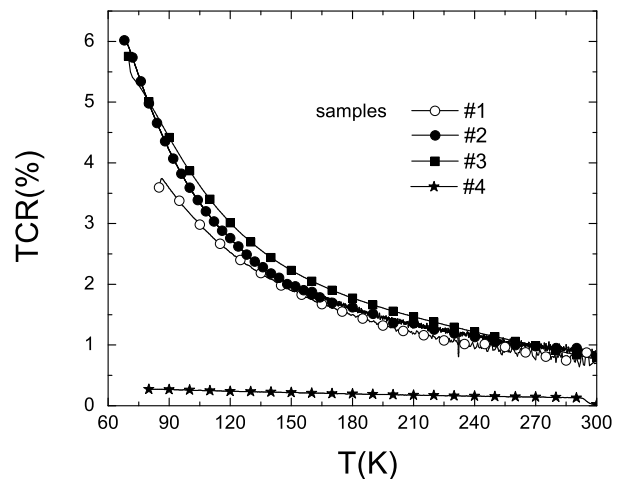


FIG. 2: TCR of the four samples versus temperature obtained by numerical derivation of the measured resistance. The value of the TCR increases from about 1% at 300K to 6% at 70K.

the temperature coefficient of resistance (TCR) given by: $\alpha = -1/R \times dR/dT$; the minus sign is only here to give a positive value for α . Indeed, the signal to noise ration in a ac calorimetry experiment is directly proportional to α . The TCR of each samples have been calculated by numerical derivation and are given in the Fig. 2. We can first notice that at 70K the TCR is up to 6% which is very

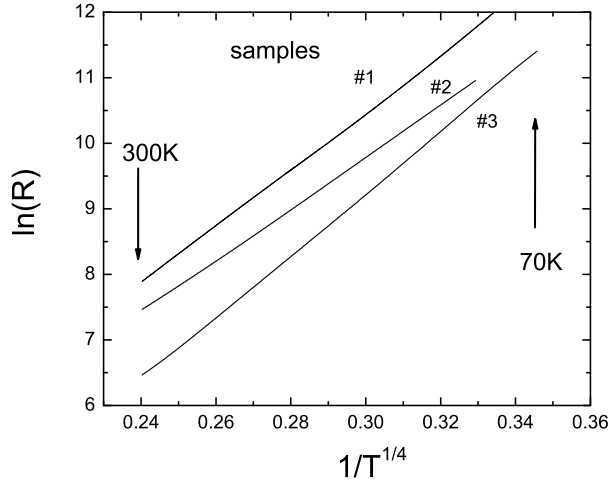


FIG. 3: The resistance of the NbN thin films are plotted on a logarithmic scale against $1/T^{1/4}$ in order to show the Mott behavior of these amorphous disordered metal-insulator materials. The reference sample #4 has not been plotted for the sake of simplicity. The behavior of $\ln(R)$ for the reference sample is almost constant in temperature at 10.2.

high when it is compared to a regular thin platinum film in which the TCR is around 1%, idem at 300K the NbN TCR is around 1% and the TCR of a thin film of platinum is not above 0.25%. Hence the performance of such thin amorphous film can be of great interest for thermometry between 70 and 300K and allows many applications for highly sensitive room temperature calorimetry. It is worth to stress that in the three samples # 1, 2 and 3, the TCR is about the same, which shows that whatever the resistance at room temperature the figure of merit is relatively constant; this is something important in terms of reproducibility. The TCR of the reference sample (#4) has been given as a comparison, it is indeed much smaller at room temperature than that of the other samples by one order of magnitude.

If the nitrogen doping is still increased a saturation in

the electrical properties is observed resulting in an increase of resistance but in no change in the temperature coefficient. This behavior is of no interest because the Johnson noise of the transducer increases with no gain in the temperature coefficient leading to a decrease of the global performances of the thermometry. The properties of these films seem comparable to what was reported about Nb-Si in reference [9]; it has been used also for calorimetric measurements up to room temperature [12]. Finally, the NbN thermometer seems at 300K a little bit less performant than amorphous YBaCuO as reported in ref [8].

In order to better describe the insulating character of the NbN thin films the resistance has been plotted on a logarithmic scale versus the inverse of temperature to the power 1/4; in the Mott law of disordered insulator the resistance is indeed given by $R(T) = R_0 \exp(T_0/T)^{1/4}$ [13] in the model of variable range hopping in three dimension samples. If the films follow a Mott law the variation of the resistance should be linear in the plot as it is illustrated in the Fig. 3. It is interesting to point out that even at high temperature this materials keeps its Mott insulator features, even if there is no current theoretical extension of this model at room temperature. Nevertheless, we anticipate no major problem prolonging the concept of Mott transition up to 300K. This confirms the origin on the increase of resistance as the temperature is lowered.

In conclusion, we are able, by increasing the number of nitrogen dopant in niobium thin film, to strongly improve the performances of NbN thermometer between liquid nitrogen and room temperature. This has been done by dragging the Mott transition up to much higher temperature. This type of thermometer will be easily implemented as transducer in micro and nanodevice in calorimetric and more generally in thermal and thermodynamic measurement for highly sensitive experiment.

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