CHEMICAL VAPOR DEPOSITION TECHNIQUES FOR THE MULTILAYER COATING OF SUPERCONDUCTING RF CAVITIES [*]

F. Weiss[†], C. Jimenez, S. Pignard, LMGP - Grenoble INP - CNRS - Minatec, Grenoble, France
M. Benz, E. Blanquet, R. Boichot, A. Mantoux, F. Mercier, SIMaP Grenoble INP - CNRS - UJF, France
C.Z. Antoine, CEA-IRFU, France

Abstract

Issued from the recent development of thin films technologies, multilayer nanostructures face today very challenging questions in materials science: ultimate size reduction, process control at an atomic scale, new size driven properties and system characterisation. For superconducting RF technologies a significant breakthrough could arise from the use of multilayered structures deposited inside Nb cavities. These multilayer nanostructures are based on the use of some 10 nanometers thick superconducting layers (d> λ L) with a higher T_c than in Nb, alternating with insulating layers, required to decouple the superconducting films. We present here our first studies devoted to nano-layered superconductors produced by Chemical Deposition techniques, CVD (Chemical Vapor Deposition) and ALD (Atomic Layer Deposition). The basic principles of CVD and ALD will be presented together with new developments of the coordination chemistry for the ALD precursors, which is key point for the optimization of the individual layers. First results concerning NbN thin films obtained by CVD to be used in Superconducting/insulating (S/I/S/I) multilayers structures are reported.

INTRODUCTION

SRF technology (RF superconductivity) has been developed by a few laboratories around the world over the past 25 years and is now widely used or foreseen for various accelerators applications, like light sources (e.g. XFEL project), or e+/e- colliders (ILC) or applications where high intensity beams require very low cryogenic losses (luminosity enhancement for LHC, high intensity protons or hadrons linacs for neutron sources or nuclear physics).

This technology is exclusively based today on bulk niobium. All attempts to use other superconductors to surpass bulk Nb have failed until now. Recent theoretical work from A. Gurevich [1–3], has given new highlights to the physical limitation of SRF. A. Gurevich has proposed a surface multilayered coating, specifically designed for RF application, able to break the niobium monopoly, and bring a significant breakthrough in SRF technology.

The multilayered structure proposed here is based on very thin NbN layers (e<10 nm) alternating with very thin AlN insulating layers (e<10 nm), see figure 1. In such a structure, the first penetration of vortices is shifted to higher

field and it can be used to screen the surface magnetic field of the cavity [1]. Recent experiments on samples with only a few layers, have shown an enhancement of the first penetration field of vortices [4–6]. In a RF cavity, at high field, the drag forces are higher than the pinning forces, and the vortex are not pinned anymore. The proper functioning regime for a cavity is the Meissner state with no vortex at all inside the cavity.

Till now, among the thin films deposition techniques used for the deposition of superconductive NbN films, physical vapor deposition methods have been almost exclusively investigated. The aim of this paper is to introduce chemical vapor deposition techniques, CVD and ALD as alternative techniques to process superconducting niobium nitride thin films. Compared to physical ones, chemical vapor deposition techniques can be used to provide films with higher purity and better conformality. Chemical Vapor Deposition technique is based on the homogeneous and heterogeneous reactions of two or more gaseous precursors that leads to the desired film deposition on the substrate surface. Atomic Layer Deposition (ALD) is based on the sequential self-limiting surface reactions from generally two gaseous precursors. It provides an ideal technique for depositing ultrathin and conformal films in 3D architectures. Main advantages of CVD and ALD vs. PVD are given in Table 1.
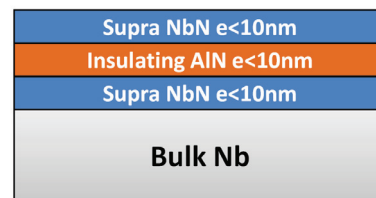

Figure 1: Targeted multilayered structure.

CVD DEPOSITION OF NBN FILMS

NbN thin films have been grown by CVD from ammonia and Nb chlorides (in situ produced). As-grown layers have been characterized by Field Effect Gun- Scanning Electron Microscopy (FEG-SEM), X-ray Diffraction (XRD) and X-ray Reflectometry (XRR). For this study, the substrates are C-plane (0001) oriented monocrystalline hexagonal sapphire. Experiments have been carried out on quarter of 2″ wafers and on whole 2″ wafers.

Table 1: PVD vs CVD vs ALD. Main Features.

PVD	CVD	ALD
Low cost	High cost	High cost
Low temperature	High temperature	Low temperature
Non uniformity	Good uniformity	Excellent uniformity
	Good conformality	Excellent conformality
High deposition rate	Average deposition rate	Very low deposition rate
Target must be tuned	Good composition control	Good composition control
	Precursor selection challenges	Precursor selection challenges
	Safety issues	Safety issues

Experimental Set-up

The HTCVD set-up consists of a graphite susceptor heated by induction in a vertical cold-wall reactor working at low pressure (Figure 2) [7]. The precursors used are ammonia, NH_3 (99,999%) and niobium chlorides, $NbCl_x$ species in situ formed via chlorination of high purity Nb wire (99,999%) with chlorine gas Cl_2 (99,999%), respectively. Before deposition process, metal wire is heated at 650°C under H_2 atmosphere in order to partially remove any native oxide. Substrates are cleaned using acetone and ethanol in ultrasonic baths. The influence of the deposition temperature on growth rate, surface morphology, crystalline state and quality of the NbN layers is studied. Deposition temperature is varied from 900°C to 1300°C.
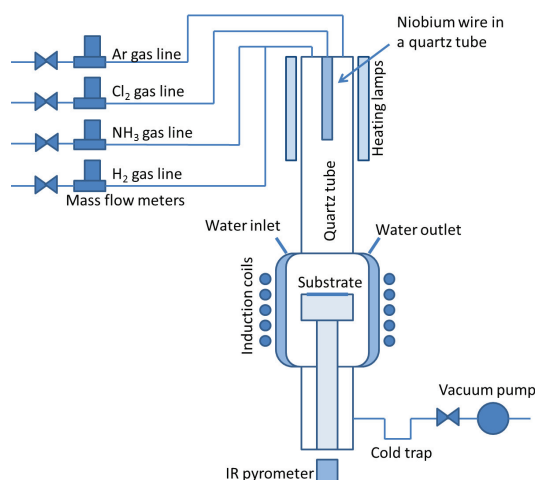

Figure 2: CVD reactor.

Results and Discussion

The NbN layers grown in this study present a homogenous specular surface with metallic reflection over a 2″ wafer. The layers exhibit no visible cracks under optical microscopy. However, the morphology and the structure of the deposited layers are strongly influenced by the deposition temperature.

Figure 3 gives the typical $\theta/2\theta$ X-ray diffraction pattern of layers deposited at 900°C and 1300°C. At 900°C, the NbN layer has a hexagonal structure (P6$_3$/mmc) with a highly (000l) preferential orientation (ICDD: 04-004-3003). However, additional peaks are observed which reveal a small polycrystalline contribution as indicated by the (10-10) and the (10-11) reflections. At 1300°C, the NbN layer has a cubic structure (Fm-3m) with a highly (111) preferential orientation (ICDD: 01-088-2404). The stability of the cubic structure at high temperature has already been discussed by Takahashi et al. [8]. However, it could also be deduced that the NbN cubic layer is polycrystalline as proved by the presence of the (200) and the (220) reflections. Additionally the peaks corresponding to (111) reflection are asymmetric. Such feature is correlated to a gradient of the lattice constant in the grown layer. The origin might have a chemical origin due to the variation of the stoichiometry of the NbN layer during the growth. It might also have a mechanical origin with the generation of stress during the growth (lattice mismatch, grain coalescence) and/or during the cooling step (difference of thermal expansion between sapphire and NbN). Such topics are under investigation. Finally, two small additional peaks are observed around 32°. They have been attributed to cubic NbN with the F-43m space group (ZB-NbN, ZB stands for Zinc-blende), but this crystal structure is metastable and remains hypothetical [9].

Figure 4 shows the as-grown surface of the NbN layer deposited at 900°C and 1300°C observed by FEG-SEM. The observation of the hexagonal NbN layer grown at 900°C reveals the presence of particles deposited on the smooth NbN surface. The particles appear like flakes and could originate from the metal wire during the cooling step. For the layer grown at 1300°C, the surface is covered by triangular- shaped grains with a typical lateral size of 20-40 nm. Some area present a different structure and are related to the (200) and (220) orientations detected by XRD (Figure 3). Furthermore, some particles appear like white dots. These particles seem to be attached to the surface and some of them present an epitaxial relationship with the underlying NbN layer. The origin of the particles is not understood yet. Finally, the thickness and the roughness of as-grown
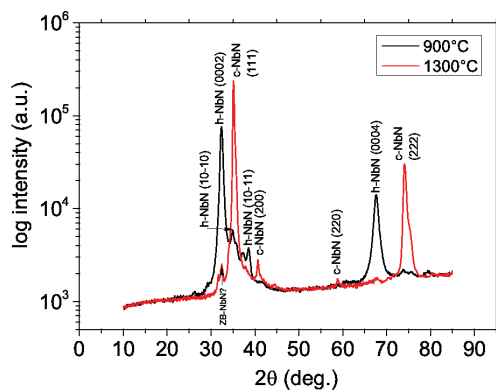
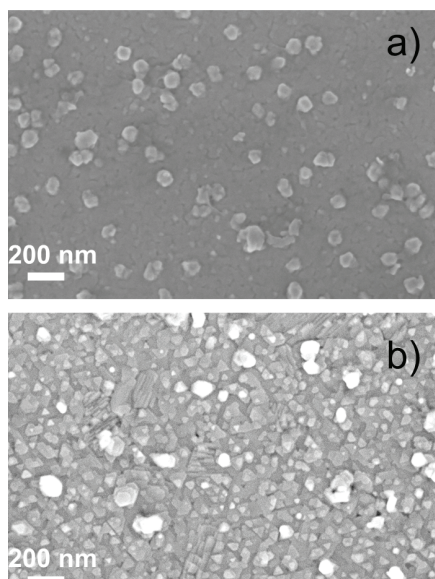Figure 3: XRD patterns of NbN thin films grown at 900°C and 1300°C.

Figure 4: FEG-SEM of as-grown surfaces. a) NbN layer grown at 900°C. b) NbN layer grown at 1300°C.

NbN layers have been measured by XRR. The thicknesses are 39 nm (which corresponds to a growth rate of 67 nm/h) and 49 nm (84 nm/h) and the roughness are 2.1 nm and 4.0 nm for the samples grown at 900°C and 1300°C respectively. An interfacial layer of Nb_2O_5 between NbN and the sapphire substrate must have been added in the simulation parameters to fit the XRR measurements. The growth rate is almost not affected by the temperature, which indicates a mass transport-limited regime for these growth conditions. The rms (root mean square) roughness for the layer grown at 1300°C has also been measured by an optical profilometer as 4.1 nm on a 1x1.4 mm^2 scan which is consistent with the value given by XRR. The increase of roughness with the temperature could be linked to either to a change of structure from hexagonal to cubic either to a transition 2D/3D growth mode. Further investigations are necessary to understand this phenomenon.

Finally the critical temperature of the film grown at 1300°C (cubic structure) is at T_c=16.6 K , This value is near the highest values reported for bulk NbN proving the high quality of our films [10].

ALD DEPOSITION OF NBN FILMS

To reach lower thermal budget while keeping the interesting conformality criteria of the above-described CVD process, ALD deposition process of NbN films will be developed. The first step will be devoted to the selection of suitable niobium organometallic precursor. Single-source precursors such as Guanidinates or Triazenides will be preferred since the number of starting precursors is reduced and they present promising physical and chemical (volatilily, stability) properties [11]. Previous laboratory experience in oxides and nitrides ALD deposition will be used [12, 13]. Definitely, ALD deposition technique will be the most adapted for the realization of multilayers inside RF accelerator cavities.

ACKNOWLEDGEMENT

CONCLUSION

40-50 nm thin NbN layers have been grown on C-plane sapphire. A change from hexagonal structure to cubic structure has been observed by increasing the deposition temperature. Very promising results regarding the critical temperature have been obtained.

REFERENCES

[1] A. Gurevich, Appl. Phys. Lett. 88 (2006) 012511.

[2] A. Gurevich, Physica C 441 (2006) 38.

[3] A. Gurevich and G. Ciovati, Phys. Rev B 77 (2008) 104501.

[4] C.Z. Antoine et al., Phys. Rev. Spec. Top. Accel. Beams 13 (2010) 121001.

[5] C.Z. Antoine et al., IEEE Trans. Appl. Supercond. 21 (2011) 2601.

[6] C.Z. Antoine et al., in SRF 2009. 2009. Berlin, Germany.

[7] A. Claudel et al., J. Cryst. Growth, 311 (2009) 3371.

[8] T. Takahashi et al., J. Cryst. Growth 46 (1979) 69-74.

[9] W. Chen et al. J. Alloys Compd., 499 (2010) 243.

[10] T. Shiino et al., Supercond. Sci. Technol. 23 (2010) 045004.

[11] N. Nimitsiriwat et al., Inorg. Chem. 46 (2007) 9988.

[12] T. Prieur et al., J. Nanosci. Nanotechnol., 11 (2011) 8383.

[13] A. Lintanf et al., Microel.Eng., 87 (2010), 373.