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Fabrication of thin metallic films by arc discharges under ultra-high vacuum conditions

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Cathodic arc deposition technology offers an excellent approach to producing pure metal, alloy and compound films at very high rates and with excellent adhesion and density. High ion energy is the main factor allowing one to produce more compact films, with much stronger adhesion to the substrate than those obtained by other methods. It was shown that the cathodic arc working in ultra-high vacuum (UHV) conditions solves the problem of the oxygen contamination originating from water vapour thus paving the road to applications where very pure metallic films are needed. The paper presents systems used for deposition of thin coatings by means of arc discharges performed under the UHV conditions. The most important experimental results and characteristics of the arc-deposited thin superconducting films are discussed, and the progress achieved recently in the formation of such films is described.

Key words: *arc deposition; metallic film; high vacuum; TiN layers*

1. Introduction

Vacuum arc deposition is one of the oldest techniques used for thin film deposition. It is often applied in the industry to deposit hard protective coatings upon cutting and forming tools as well as decorative coatings such as golden-colour TiN layers. Moreover, this technique may also be used for more demanding technological applications in optics and electronics. The interest in vacuum arc evaporation arises primarily from the nature of the arc discharge plasma and its properties in relation to high qual-

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ity film growth. In principle, this phenomenon is a plasma discharge between two metallic electrodes under vacuum. It is usually characterized by a low-voltage (20–40 V), high-current discharge (50–200 A) initiated under high vacuum (10^{-9}–10^{-10} mbar) and taking place in vapours of the cathode material [1]. High deposition energy of the condensing species is essential for the film growth and promotes adhesion as well as disruption of columnar growth. Furthermore, estimates of energies required for the high quality film growth, which are based on ion-surface interaction models, indicate that energies of the order of 25–100 eV are also desirable for activating surface atom displacements and maintaining good crystallinity of the underlying bulk layers. Unfortunately, this technique is plagued by macro-particles emitted from the cathode surface which are deposited onto the substrates and consequently deteriorate uniformity of the film. The dimensions of macro-particles are usually within the range of 0.1–10 μm. In order to eliminate the micro-droplets from vacuum-arc plasma and in consequence from the deposited film, one can apply various magnetic filters.

Within a frame of the Coordinated Accelerator Research in Europe (CARE) program (concerning the construction of large linear accelerators), a research group from the IPJ Swierk, Poland achieved a considerable progress in the development of the cathodic arc technology [2]. The main activity of this group is concentrated on the deposition of thin pure metallic films. Such layers can reveal their superconducting properties after cooling down to cryogenic temperatures, and they can be applied as new approaches in accelerator technologies. The deposition of the superconducting thin films is not a trivial issue. Some metals (like Nb and Pb), revealing superconductivity in the bulk forms, sometimes do not demonstrate such properties when they are used in the forms of thin layers. There are two main factors which can influence the layers superconductivity: a good quality (mainly density and surface homogeneity) and their very high purity. In order to fulfil the above requirements, a new concept of the deposition of thin super-conducting layers by means of arc discharges under ultra-high vacuum (UHV) conditions, has been developed. This new approach may solve the problem of elimination of contaminations originating from residual gases in a vacuum chamber. Moreover, the UHV arc technique of thin film deposition enables high quality and surface homogeneity to be achieved.

The main aim of this paper is to describe various UHV facilities designed and tested at the IPJ Swierk, Poland. Another aim is to show examples of the deposited metal (Nb and Pb) layers and to present results of the investigation of their morphological and structural characteristics as well as their possible applications in nanotechnology.

2. Experimental

It should be noted that very low pressures can be achieved only when all parts of the deposition system are designed and built in accordance with the UHV technology requirements. In our case, all the vacuum chamber components and accessories, as well as all vacuum connections, were manufactured using only high purity materials:

stainless-steel, oxygen-free high conductivity (OFHC) copper and high-quality ceramics (shielded from the arc). Our UHV arc facility was equipped with an oil-free pumping system consisting of a two-stage fore-vacuum pump and a turbo-molecular pump. It allowed one to reach a basic pressure lower than 10^{-8} mbar after 24 h of baking at 150 ºC. The reliable triggering (ignition) of arc discharges is often a serious problem, even in the industrial arc-based devices. In HV systems, thin layers of gases and impurities that are formed upon the surface of electrodes, facilitate the starting of an arc discharge. Under UHV conditions, high-temperature baking of the vacuum chamber reduces thickness of such layers. The described effects, as well as requirements that all other sources of impurities must be eliminated, make the arc ignition more difficult. After testing many triggering methods from the point of view of the operational reliability and cleanness, we have finally decided to use a laser beam, introduced through an appropriate vacuum-tight glass window, and focused upon the cathode surface. Under such conditions the arc discharge can be triggered extremely reliably without introducing any additional impurity. Our arc sources have been equipped with Nd:YAG lasers (532 nm, 50–100 mJ, 10 ns), and the mastering of the laser ignition technique appeared to be decisive for improving properties of the deposited layers.

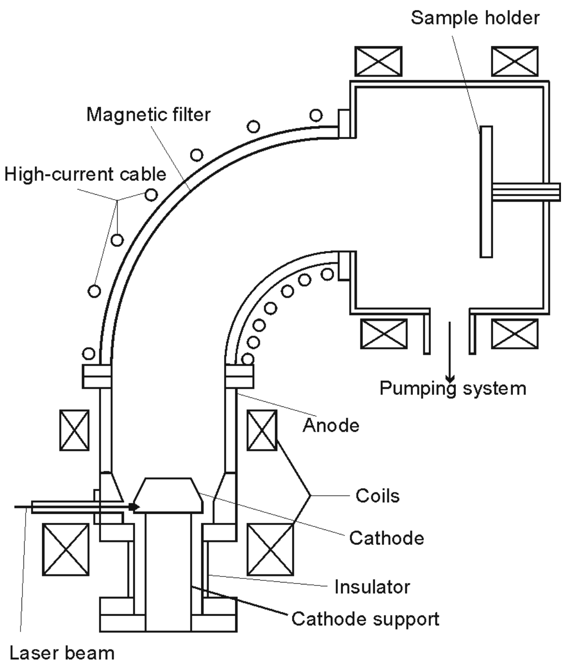

Fig. 1. Scheme of a UHV arc facility with a planar cathode and a knee-type magnetic filter

In the performed experiments, the used set-up was made of a plasma arc source equipped with a truncated cone cathode (Fig. 1). The cathode was fixed upon a water-cooled support placed inside a vacuum chamber. The lowest possible arc current for stable operation in the DC mode was found to be about 60 A for the cathode made of niobium and 23 A for that made of lead. The cooling system of the anode had an upper limit of an arc current equal to about 140 A. To eliminate the micro-droplets deposition on the substrate, a magnetic filter was applied, deflecting arc plasma whilst the micro-droplets were caught upon walls. Two knee-type filters, as well as a T-shaped filter have been designed for the microdroplets removal. All of them based on water cooled tubes equipped with CF100 flanges. The knee-types filters differed in the curvature radii. The applied magnetic field deflected ion trajectories and let them pass along the knee- or T-shaped filters, while the microdroplets could be collected upon the filter walls. The magnetizing current was drawn through windings made of a copper cable wrapped around the filter channel. In the T-shaped filter, an additional coil was applied in the branch region in order to assure a smooth bending of the magnetic field lines. The samples were mounted upon a sample holder consisting of a massive copper (OFHC Cu) flange (Fig. 1).

The substrates for coating were mounted upon a holder fixed to the electrically insulated copper flange. That enabled bias voltage to be applied and due to heat exchange assured a stable temperature during the deposition process. In order to increase ion impact energy, bias voltages (from –20 V to –200 V) were applied to the substrate in a DC or kHz frequency mode. The facility enabled several substrates to be coated simultaneously. A detailed description of the planar arc facility constructed at IPJ Swierk can be found elsewhere [2–5].

3. Formation and properties of UHV arc deposited metallic thin films

3.1. Formation of Nb and Pb films

During a single deposition process, four substrates were coated simultaneously, e.g. Nb/Cu, Nb/sapphire, Pb/Cu and Pb/sapphire. The sample temperature was changed from room temperature up to 250 °C at the end of the process. For all samples the –70 V bias voltage was applied and the deposition rate with the system operated with arc currents of 80–100 A, was about 1 nm/s. The rise of pressure from the base value to 10^{-6} mbar was observed when the arc discharge was started. After that, the pressure stayed almost stable at the latter value throughout the whole deposition process. In situ mass spectroscopy showed that the gas pressure rise during the arc discharge was almost exclusively caused by hydrogen. Its partial pressure was more than 3 orders of magnitude higher than that of other contaminants.

3.2. Superconducting properties

Resistance of thin Nb films was measured from room temperature to about 4 K in order to observe the transition to the superconducting state ($T_c \sim 9.5$ K) and to determine the residual resistance ratio (RRR) between 300 K and 10 K (i.e., just above T_c).

Both parameters are related with superconducting properties and are very sensitive to impurities. For these measurements, the standard four-lead method was applied with a dc current changing from 2 mA to 200 mA, depending on the resistance and thus on temperature. Four Cu leads were attached to the Nb film with a silver paint. Attention was paid to keep dimensions of the voltage contacts at least 10 times smaller than the distance between the Cu leads. This allowed one to measure the RRR with the precision better than 1% and to calculate the resistivity with the accuracy better than 10%, if the thickness of the film was known. RRR values, measured for 1.5 μm-thick Nb films under typical UHV conditions described above, ranged from 30 to 50.

3.3. Film structure

The crystalline structure of niobium films grown on the grounded and biased single-crystal sapphire (001) substrate has been studied in order to identify the parameters determining the resulting film structure. The application of –70 V bias potential makes the ion impact energy almost twice higher as compared to the case of the grounded substrate. It enhances the surface and in-depth diffusion.

X-ray diffraction measurements in the (θ–2θ) mode have been performed with the monochromatised $CuK_{\alpha 1}$ radiation. Obtained diffraction patterns show broadened reflections originating from the deposited Nb layer, accompanied by strong and narrow reflections associated with the substrate. For both samples, the Nb 110 reflections have been found 10^3 times stronger than intensities expected for the powdered niobium. That indicates the dominating out of plane orientation of the niobium <110> crystalline axis. This orientation results from the intrinsic properties of Nb the films which are enhanced by the interaction with the substrate. An epitaxial relation between sapphire and Nb has been studied in [7, 8].

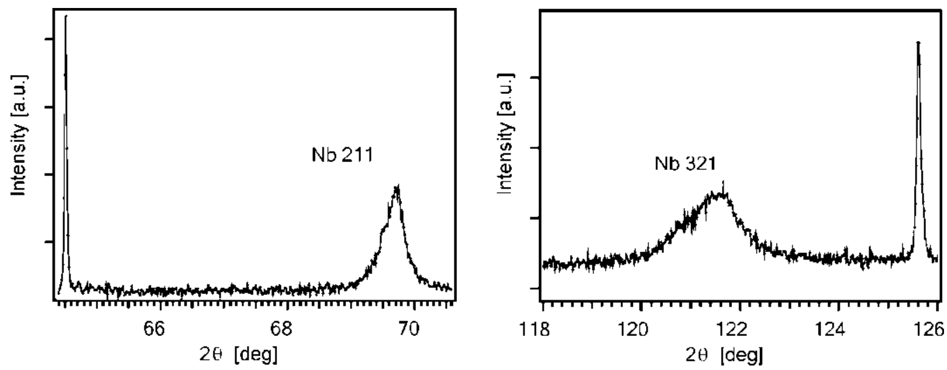

Fig. 2. Distinctive peak profiles observed for Nb 211 and 321 reflections

A comparison of the Nb reflections in diffraction patterns, as measured for two samples, reveals shifts in the angular position and different shapes of the peak profiles. The most pronounced differences occur for 211 and 321 reflections and which are asymmetric. The other ones are symmetric and differ slightly in FWHM. The most distinctive features of diffraction patterns as measured for polarized and grounded samples are shown in Fig. 2.

The out of plane lattice parameters have been evaluated based on angular positions of the Nb reflections. They are 3.3032±0.003 Å and 3.3017±0.003 Å for the sample grown on the biased- and grounded-substrates, respectively. The obtained values are higher than 3.3004 Å reported for Nb bcc bulk. The structural distortions are different for the two investigated Nb/sapphire films. The observed differences in peak profiles point out that the lattice expansion is not uniform in the whole depth of the layer. The region affected by changes is in both cases wider than the Nb/sapphire interface. The diffraction pattern was measured for the Nb film deposited upon the electropolished copper substrate. None of the profile shape modifications observed for the Nb/sapphire diffraction pattern can be identified in that case. All niobium reflections are symmetric, much wider and shifted comparing to those observed for the Nb/sapphire.

The performed studies showed that the interaction of a sapphire single crystal substrate with the growing Nb layer modifies the resulting film structure. It leads to a strong texture and lattice distortion. On the other hand, the structure of the Nb film grown on the electropolished copper polycrystalline substrate is relaxed and closer to that of Nb bulk. Evidences for a weak influence of ion impact energy on the film structure have been found. The XRD analysis of thin Pb films deposited by means of the UHV arc technique is under preparation.

3.4. Surface morphology

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were applied for the surface quality inspection in search of small-scale defects and for the observation of the surface structure. Figure 3a shows a SEM picture of the deposited Nb layer. One can easily see a lack of micro-droplets upon the surface what confirms the effective plasma filtering. Moreover, the longitudinal shape of surface grains is clearly visible. The roughness of the Nb films deposited upon sapphire substrate was found to be of the order of few tens nanometers. A SEM picture of the Pb film surface is shown on Fig. 3b. The surface is also a very homogeneous and dense one.

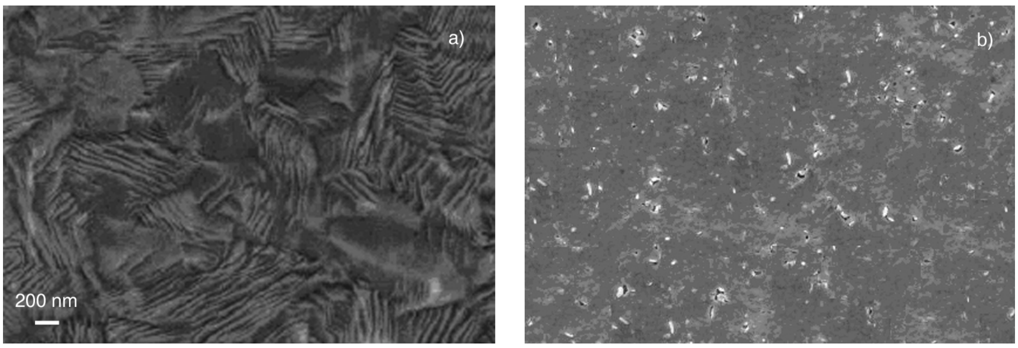

Fig. 3. SEM pictures of the surface of Nb (a) and Pb (b) films

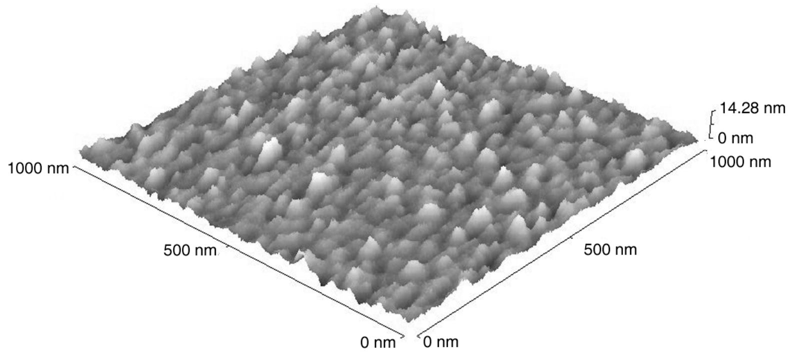

Fig. 4. AFM image of the thin Nb film

Additional data on the quality of the deposited thin Nb films has been obtained using the atomic force microscopy (AFM) technique. The AFM image of such a film is shown in Fig. 4. The measured values of the roughness of the deposited Nb film were below 20 nm. Moreover, a good quality of the film as well as good plasma filtering were confirmed.

3.5. Film purity

Information about the surface chemical composition and depth profiles of Nb and Pb layers were obtained by means of a time-of-flight (ToF) SIMS mass-spectrometer. Secondary ions emitted from the bombarded surface were mass-separated and counted with the ToF analyzer. Results of the depth profiles measurement are presented in Fig. 5.

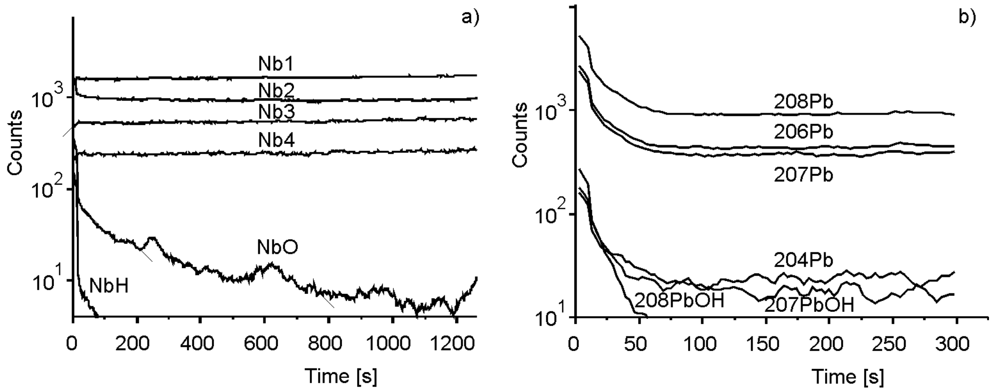

Fig. 5. Results of SIMS measurements of the deposited Nb (a) and Pb (b) layers

One can easily see that the deposited layers consisted mainly of the pure metals. The presence of some heavy impurities (like Na and K species) has also been observed but their amounts were very low (not shown in this scale). A characteristic feature of the deposited layers is a relatively high level of oxidation in the near-surface region which probably originates from the atmospheric oxygen diffusion.

4. Conclusions

The UHV cathodic arc deposition technique has been successfully applied to obtain high purity superconducting layers of niobium and lead. The deposition of micro-droplets from vacuum-arc plasma has been avoided by the application of the especially designed and tested filters.

The reported XRD, SEM, AFM and SIMS studies showed unanimously that the impurities concentration in the obtained Nb and Pb films is satisfactorily low. The achieved cleanness goes together with outstanding superconducting properties. It opens a new road to many applications where dense, high-quality and very pure metallic films are needed, e.g. in micro-electronics, nanotechnology, medicine etc.

Acknowledgement

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