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APPLICATION OF A dc GLOW DISCHARGE FOR NbN FILMS CREATION[1])

J. KODYMOVÁ[2]), V. KREJČÍ[2]), L. LÁSKA[2]), J. VOTRUBA[2]), Prague

Niobium nitride film creation by means of a dc discharge technique has been investigated. Scanning electron micrographs of the modified substrate surfaces are presented.

ПРИМЕНЕНИЕ ТЛЕЮЩЕГО РАЗРЯДА ОТ ПОСТОЯННОГО ТОКА ДЛЯ ОБРАЗОВАНИЯ ПЛЕНОК NbN

В работе приведены результаты исследования образования пленок нитрида ниобия при помощи тлеющего разряда от постоянного тока. Продемонстрированы также электронномикроскопические снимки модифицированных поверхностей.

I. INTRODUCTION

Plasma treatment of metals resulting in the nitride film creation on their surfaces has been recently much investigated. Such a surface modification is very useful for many technological applications because of advantageous physical and chemical properties of nitrides. Transition-metal nitrides, such as NbN, are characterized by their superconducting properties, namely by the critical current density ($J_c \sim 10^5$ A/cm^2 at 100 kOe), the upper critical magnetic field ($H_c \sim 200$ kOe) and extremely high transition temperatures ($T_c \sim 16$ K) e.g. [1—5]. The process of niobium nitridation resulting in the production of the requested superconducting films is complicated by the fact that the Nb-N phase diagram is very complex and NbN_x exists over a wide range of compositions [3, 4]. It is evident from Tab. 1 that the superconducting phase of interest in the Nb-N system is the face centred cubic (fcc) or δ-phase and that the superconducting properties are considerably affected even by slight variations in the composition and hence by little changes of experimental conditions during its preparation. Especially the optimum partial

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[2]) Institute of Physics, Czechosl. Acad. Sci., Na Slovance 2, 180 40 PRAGUE, Czechoslovakia.

pressure, substrate temperature and discharge current must be experimentally determined for obtaining the maximum T_c [6]. To prepare these films the rf or ac sputtering methods have been most frequently used e.g. [1—6]. Such thin films are usually deposited on glass substrates.

A further possibility of the low temperature process (up to 600 °C) for NbN films creation could be direct nitridation of Nb samples which serve simultaneously as the active electrodes of a discharge in nitrogen. This technique, which has not yet been used for NbN preparation, has some advantages. It enables to obtain in one experiment films created at considerably different substrate temperatures (on the cathode and the anode); moreover, specific discharge particles are involved in the growth mechanism [7]. It can be expected that the films will exhibit better mechanical properties, especially adhesion, because they grow directly from the Nb substrate. The aim of our experiments was to explore these possibilities and qualitatively compare the films formed on the anode and cathode of a dc glow discharge with those sputtered from the cathode on a neutral electrode.

II. EXPERIMENT

The experimental work was performed on a similar apparatus as that used for the study of magnesium nitriding, e.g. [8]. Samples of polycrystalline Nb cut from Nb sheet were in the form of square specimens 5 × 5 mm. The sample holders made of molybdenum shielded with glass were used also for the power supply. The distance between the anode and cathode was 15 cm, the sample which served as a substrate for sputtered nitride was located 6 mm behind the cathode. The diameter of the discharge tube was 6 cm. The surface of specimen was chemically cleaned in a mixture of H_3PO_4 (65 %) + HF (48 %) + HNO_3 (65 %) (1 : 1 : 1) for about 5 minutes and then rinsed in methanol [9]. Prior to plasma nitridation the samples were subjected to the argon discharge for about 10 minutes. The measurements of the nitridation were performed in a sealed system at the pressure of spectroscopically pure nitrogen of 650 pascals and the discharge current of 15 mA maintained electronically at a constant value for the experimental time of 24 hours.

III. RESULTS

We used scanning electron microscopy as the diagnostic method. It enables us to indicate the surface changes of Nb owing to plasma treatment and to compare the surface modifications of the particular samples. However, it does not make possible to determine the value of x in the NbN_x, that means, to decide if the obtained nitride was the required superconducting δ-NbN phase or not. Measurements of magnetization curves which should give us this information are in course.

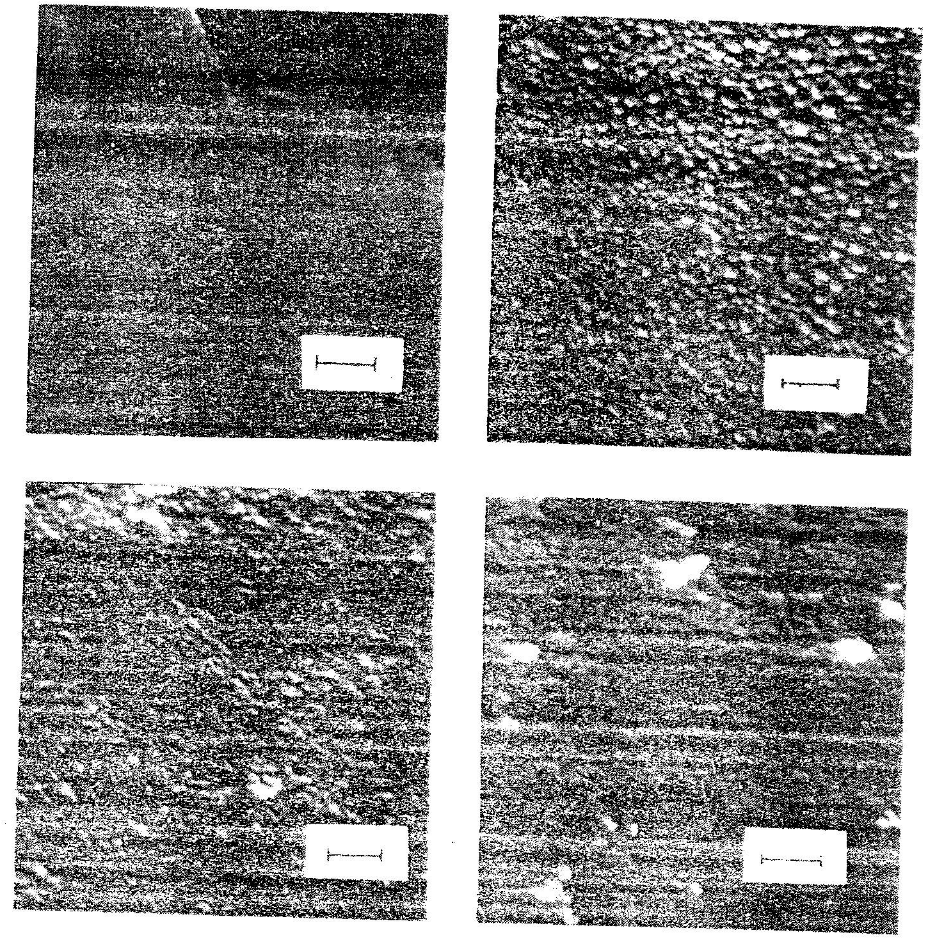

Fig. 1. Scanning electron micrographs a) of the pure Nb surface, b) of the sputtered film and of the films created on c) the anode and d) the cathode of the discharge (the line segment in all Figs. represents 10 μm).

In Fig. 1a there is the scanning electron micrograph showing the surface morphology of the pure Nb sample before nitridation. The structure of an NbN_x film produced by sputtering from the cathode on Nb substrate is shown in Fig. 1b. It can be seen that NbN_x consists of spherical balls each composed of much smaller microcrystallites. This crystallic structure is very similar to that presented in [10] for compact NbN produced by spray-dried-power and sintering techniques. The superconducting properties of such NbN correspond to the δ-NbN phase. A somewhat different surface morphology have the NbN_x films created on the anode (Fig. 1c) and on the cathode (Fig. 1d). They seem to be more homogeneous with a tendency to copy a crystalline structure of the original metal. Comparing them with the surface structure of Nb (Fig. 1a) or with Fig. 1b we can therefore expect that the direct nitridation of Nb by this method could be advantageous for some technical applications.

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Table 1

Stoichiometry, structure and superconducting transition temperature of the stable NbN_x phase [3, 4⁺]

Phase	α-Nb	β-Nb_2N	γ-Nb_4N_3	δ-NbN	ε-NbN
Composition ratio of N/Nb	<0.4	0.40—0.52	0.75—0.80	0.88—0.91 (1.015—1.062)⁺	0.92—1.00
Structure	interstitial nitrogen in Nb lattice	hexagonal	tetragonal	cubic	hexagonal
T_c(K)	strong function of x	1.94	7.2	16.1	1.94

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