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Transverse transmission electron microscopy of sputtered NbN films

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A technique of preparing transverse sections of sputtered NbN films for transmission electron microscopy is presented. Microstructural details of grain morphologies, orientations, and phase compositions can be readily analysed using transverse specimens over the entire film thickness including the deposited film–substrate interface.

1. Introduction

The rapid growth of the film deposition processes (i.e. chemical vapour deposition and sputtering) in the semiconductor, and more recently in the superconducting fields has also led to an increased interest in microstructural details of thin solid films [1]. With the advent of transmission electron microscopy (TEM), many important features of deposited films such as fine grained structures and defects are made observable because of the higher spatial resolution. With appropriate instrumentation, the transmission electron microscope is capable of chemical and phase analysis by measuring X-ray fluorescence, electron energy loss (EELS), and with microdiffraction techniques.

Traditionally, TEM specimens of deposited films have been planar sections (i.e. the electron beam is perpendicular to the plane of the film), and although much microstructural detail can be observed, conventional planar specimens cannot easily provide information on the variation of grain morphology and orientation, local chemistry and grain growth kinetics as a function of distance from the substrate. Studies of adhesion of deposited films to the substrate are not possible with planar sections. In light of this, we have prepared *transverse* sections of deposited films for transmission electron microscopy. This paper demonstrates the usefulness of this preparation technique as a means to determine the detailed microstructure of films of NbN and to correlate it with the sputtering conditions and superconducting properties [2–4] (see Table I).

2. Preparation of transverse microscopy sections

The technique of preparing transverse microscopy sections as developed by King *et al.* [5] is outlined in Fig. 1. The specimen is cut into strips approximately 3 mm wide, and sandwiched together with a silver epoxy–hardener mixture (Epotek H20E) such that the film sides are facing one another. This rectangular specimen block is set in a stainless steel tube (~ 3 mm inner radius), which is filled with an epoxy–hardener mixture (Hardman). The NbN film sides are thus situated in the centre of the 3 mm cyclinder. The specimen cylinder is then epoxied into a larger stainless steel tube for slicing into 400 to 500 μm sections. The transverse sections then undergo the following thinning procedure:

1. Mechanical polishing; the transverse specimens are reduced to a thickness of ~ 100 μm.
2. Dimpling; a circular pit is formed at the centre of the disk using a VCR group dimpler (Model D500). The thickness of the film at the centre of the dimple is approximately 15 to 25 μm thick.
3. Ion milling; the specimen is placed in an ion mill (Ion Tech) until a hole is produced within the dimpled area. The surrounding areas of the hole are electron transparent thus providing areas for analysis.

3. Microstructure

Fig. 2 is a bright field (BF) transverse micrograph of NbN grains near the film–substrate interface of film A. The transverse micrograph shows a columnar microstructure of the NbN grains surrounded by well-defined intergranular regions (1 to 3 nm in width) that appear bright in the micrograph. It has been shown that the growth is preferentially in a [1 1 1] direction of its f c c structure [2]. A columnar structure is typical of sputtered films deposited at temperatures well below their melting point [6]. The existence of well-defined intergranular regions in NbN was first proposed by Wagner *et al.* [7] while Gavaler *et al.* [8] suggested that this columnar–intergranular structure may play an important role in determining the superconducting properties. Note that the grains do not appear

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TABLE I Deposition conditions (argon and nitrogen partial pressures, sputtering rate and substrate temperature), film thickness, and superconducting properties (critical current density at a 19 T parallel field, upper critical field (parallel) at 4.2 K and critical temperature) of the transverse section samples described in this paper.

Substrate	Film A (8405) sapphire	Film B (8535) sapphire	Film C (8539) sapphire	Film D (8442) Hastelloy
P_{Ar} (mtorr)	6.1	25.2	35.3	12.3
P_{N_2} (mtorr)	1.4	2.1	2.3	1.6
Rate (nm sec^{-1})	1.04	5.1	5.1	1.25
T_{sub} (°C)	150	290	300	425
Thickness (μm)	1.7	3.0	3.0	2.2
$J_{c\parallel}$ (19 T, 4.2 K) [A mm^{-2}]	< 10	61	110	
$H_{c\parallel}$ (4.2 K) [T]	18	23.8	23.8	
T_c (K)	11.2	14.9	13.3	

structurally homogeneous – some grains contain a predominance of darker contrasting areas while others contain lighter contrasting areas. These dark areas are thought to be either the result of misorientation of the grains (grains tilted at some angle to the [1 1 1] direction) or due to NbN crystals within the grains oriented in a non-[1 1 1] direction (i.e. [2 0 0], [2 2 0] direction etc.). The composition of the intergranular regions is as yet undetermined and further analytical experiments such as EELS are planned.

The transverse micrograph also shows details near the film substrate interface revealing how the columnar microstructure develops as the film grows. In the first 100 nm above the film–substrate interface there exists a transition region in which the NbN grains and intergranular regions grow in many directions relative to the substrate surface. Beyond a film height of 100 nm, a distinct columnar grain structure is seen and the NbN grains and intergranular regions are aligned approximately perpendicular to the substrate (see also Fig. 6).

Fig. 3 is a BF transverse micrograph of NbN grains taken in the middle portion of NbN film B. The transverse section shows a more parallel orientation of the columnar grains than for film A, and the columnar grains are again surrounded by intergranular regions 1 to 3 nm in width. The selected area diffraction pattern (SADP) of the columnar grains (Fig. 4) shows the grains to be polycrystalline and the diffraction pattern can be indexed to f c c NbN. The intense spots on the (1 1 1) ring indicate again that the growth axis of the columnar grains is in the direction of [1 1 1]. There also appears to be texturing along [2 0 0] and [2 2 0] directions in some grains.

There are some rather interesting features of this film not seen in film A. Several areas show little evidence of intergranular regions and there appear to be intergranular regions within some grains which are at random angles to the [1 1 1] growth direction. It should also be noted that the grains contain cracks running across the columnar grains. These cracks lie at angles of ~ 55° with respect to the [1 1 1] direction suggesting they lie along {1 0 0} cleavage planes. It is

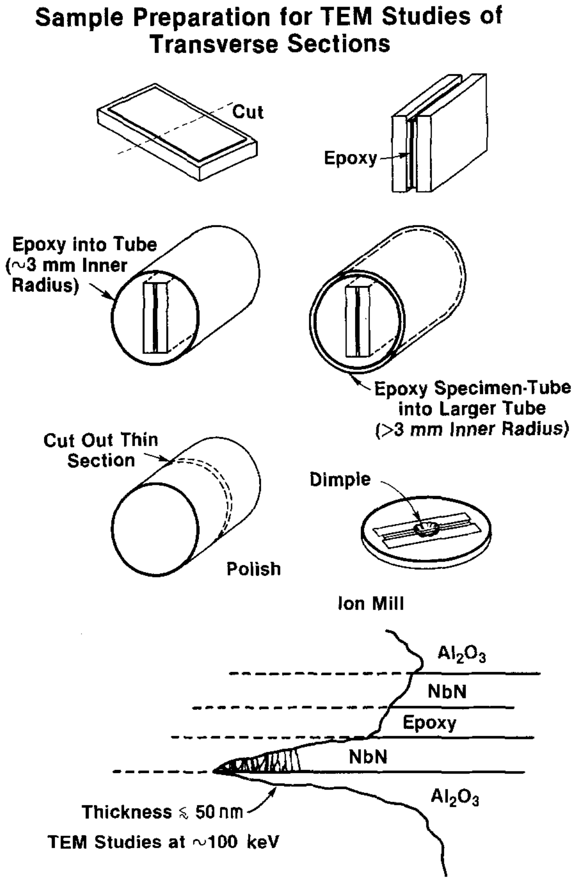

Figure 1 Schematic outline of transverse section specimen preparation for TEM.

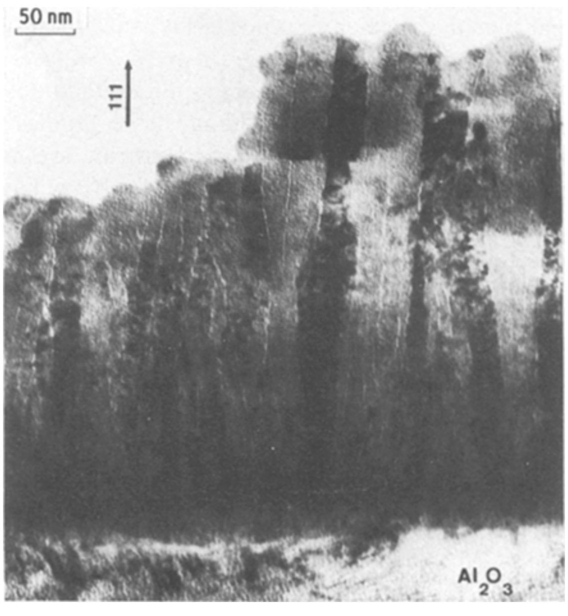

Figure 2 Bright field transverse micrograph of film A [NN8405] showing NbN columnar grains near film–substrate interface.

Figure 3 Bright field transverse micrograph of film B [NN8535] showing NbN columnar grain in the middle portion of the film.

as yet undetermined whether these cracks are intrinsic to the film itself or are effective to the ion milling process; further experiments are planned to determine this.

Fig. 5 is a transverse micrograph of film C which shows a large section of the film's columnar microstructure from the film–substrate interface throughout the entire film thickness. The micrograph shows that although the columnar grain structure exists, there also appears to be an extensive amount of intergranular regions within the grains residing at random angles to the [1 1 1] direction. The intergranular regions also are less distinct and much more disorganized in appearance, possessing jagged features. The widths of these intergranular regions are again measured to be 1 to 3 nm. Note that the structure of this film in particular is reminiscent of, and not inconsistent with, dendritic growth.

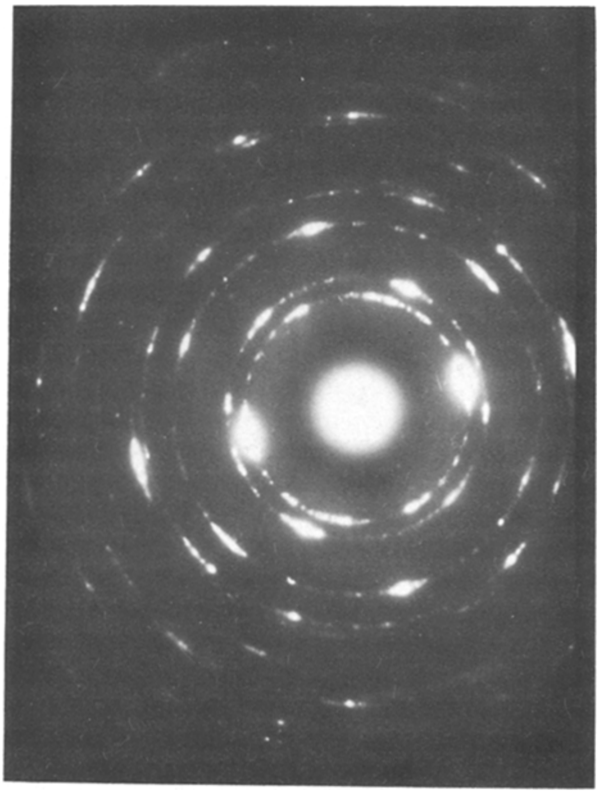

Figure 4 Selected area diffraction pattern of NbN columnar grains in Fig. 3.

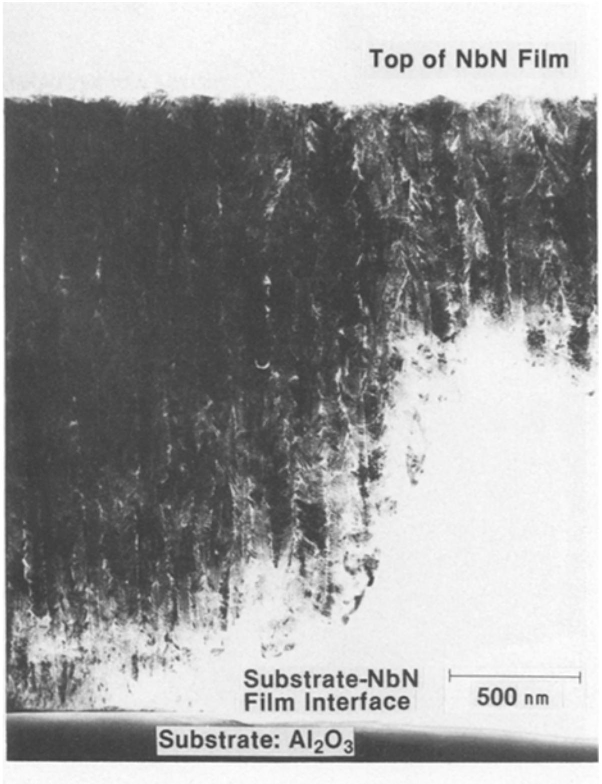

Figure 5 Bright field transverse micrograph of film C [NN8539] showing entire NbN film.

Fig. 6 is a higher magnification picture of NbN grains at the film–substrate interface of sample C. The micrograph reveals that the grains initially grow in many directions relative to the substrate, as was the case for film A in Fig. 2, but with a higher concentration of grains starting from the substrate. This transition region in film C extends to a height of ~ 50 nm, compared to ~ 100 nm for film A. Beyond the transition region, a columnar grain structure is again observed and continues through the entire thickness of the film. The SADP for film C shows the grains to be for the most part polycrystalline NbN, with preferential orientation along the [1 1 1], [2 0 0], and [2 2 0] directions. There is, in addition, a faint halo present around the beam spot inside the (1 1 1) ring which suggests that some portions of the film are amorphous.

4. Grain size determination

Unique to transverse microscopy sections is the possibility of studying the grain morphologies near the film–substrate interface as well as throughout the thickness of the film. In addition, transverse microscopy

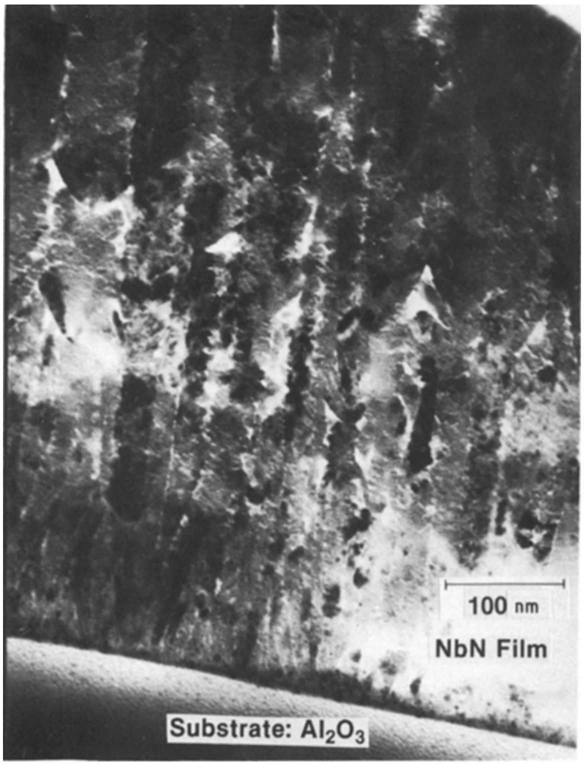

Figure 6 Bright field transverse micrograph of film C [NN8539] showing NbN grains at film–substrate interface.

sections allow for accurate measurements of the grain diameter as a function of film height. Fig. 7 is a plot of the average grain diameter determined by the linear intercept technique, as a function of distance from the substrate for several sputtered NbN film samples. All 4 specimens show similar grain growth patterns even though they were prepared under quite different sputtering conditions and exhibit considerably different superconducting properties (see Table I). For the first 600 nm, where data was obtained on all 4 specimens, there is a surprisingly universal linear increase in average grain size. The saturation of NbN grain size with increasing thickness above the substrate, which has been reported by others [9], is not found by us as can be seen for film C where we have data for almost the entire film thickness. Grain diameter measurements, near what was believed to be the top of the film, were also made on films B and D. They tend to confirm the suggestion of an approximately linear grain growth throughout the entire thickness.

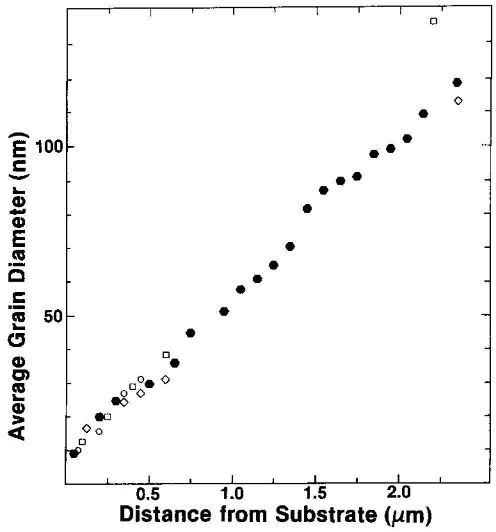

Figure 7 Plot of average grain diameter as a function of distance from the substrate for films A to D. (●) A; (◇) B; (○) C; (□) D.

5. Conclusions

Examples of microstructural analysis of deposited NbN films utilizing transverse transmission electron microscopy sections have been presented. These results demonstrate the main advantage of transverse sections as opposed to planar sections: the variation of microstructure as a function of distance from the substrate can be analysed directly and in greater detail. For example, analysis of grain structures and orientations, as well as phase compositions within grains, can be realized throughout the film thickness. In addition, direct observations of the grain morphologies within the narrow transition region at the substrate interface we can give insight into the grain growth kinetics during the initial formation of the film. Thus, this technique is very promising for detailed studies of the interrelationships of sputtering parameters, growth morphology and superconducting properties. Such a study will be the subject of future publications.

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