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# Microstructure and superconducting properties of $MgB_2$ films prepared by solid state reaction of multilayer precursors of the elements

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ABSTRACT

Surface morphology and superconducting properties of $MgB_2$ superconducting thin films prepared by ex-situ annealing of multilayer Mg/B precursors in Mg vapor are studied.
Depending on the precursor structure different physical and microstructural properties of the superconductor evolve. Structure and composition of the films are analyzed by scanning electron microscopy and wavelength dispersive x-ray spectroscopy. It is found that certain precursor structures can lead to high quality superconducting films, however, in specific precursor structures mechanical stress leads to the formation of wrinkles strongly affecting the superconducting homogeneity of the films. A correlation between microstructure and superconducting properties, such as pinning or critical current density, can be provided via magneto-optical Faraday microscopy.



## 1. Introduction

Thin magnesium diboride films are highly attractive for superconducting applications since they exhibit the highest critical temperature of all simple metallic compounds. Nearly anisotropic superconducting properties, robustness against the presence of grain boundaries [1] and high ductility allowing good mechanical deformation are advantages that cannot be provided by any material with higher superconducting transition temperatures such as the cuprates or the pnictides [2]. However, the preparation of $MgB_2$ thin films with reasonable properties is a task not easy to cope with.

The preparation out of the elements is difficult because of the extremely different vapor pressures of magnesium and boron. A stoichiometric driven process often lacks magnesium escaping during the process, which in the end leads to boron-rich phases such as $MgB_4$. A comprehensive review on possible solutions for adequate preparation paths is given by Naito and Ueda [3]. In this paper we follow the route of depositing a Mg/B multilayer precursor which is then post annealed in Mg vapor at high temperatures. This process leads to $MgB_2$ films with transition temperatures between $T_c = 30$ K and $T_c = 35$ K exhibiting high critical currents of up to $j_c = 10^{11}$ A/m$^2$ at $T = 10$ K [4,5]. However, it turned out that the process is extremely sensitive to both precursor structure and substrate properties.

In this paper we present an analysis of superconducting $MgB_2$ films that have been prepared from different precursor multilayer sequences. We show that changing the substrate near layer from magnesium to boron leads to a completely different microstructure of the finally produced superconducting film. In one case homogeneous films are obtained exhibiting consistent superconducting properties. In the other case, a strong distortion of the superconducting layer takes place which leads to highly inhomogeneous films.

## 2. Sample production process

$MgB_2$ films have been prepared by Mg/B – multilayer electron beam evaporation on r – cut $Al_2O_3$ substrates and a subsequent ex-situ annealing process [4–6]. The precursor contained a first layer of 30 nm Mg followed by four times the combination (B 30 nm/Mg 60 nm). In order to investigate the role of the multilayer sequence we used an incomplete initial magnesium layer, which is only covering the inner part of the substrate. This allows the comparative analysis of two precursor scenarios on one identical substrate and at the same external conditions. Afterwards the following annealing process was carried out in an atmosphere of Argon for 30 min at 700 °C. Typical resulting $MgB_2$ films are $5 \times 5$ mm in size, have a thickness of approximately 300 nm. It is worth mentioning that both substrate material and crystallographic orientation of the surface severely influence the superconducting properties of the films. Best results have been obtained in the above described manner.

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Fig. 1(a) displays an optical micrograph of a $MgB_2$ film prepared using an incomplete initial magnesium layer. Easily two different areas can be identified. A horizontally oriented strip in the center separates the areas above and below exhibiting a different optical appearance. Larger magnifications offer an impression that the part in the center of the film seems to be very homogeneous whereas the adjacent regions above and below look rather rough and inhomogeneous. A sketch depicted in Fig. 1b illustrates the distribution of different film areas. The microstructure is enlarged in the sketch for better clarification.

## 3. Microstructure analysis

To get a deeper insight into the microstructural properties of different regions of the film we characterized the samples via scanning electron microscopy (SEM) which is installed within a *Nova NanoLab 600 DualBeam*. The SEM images were taken with scattered electrons with an accelerating voltage of 5 kV and a beam current of 0.4 nA. The electron beam was at an angle of 52° to the vertical, thus it is possible to view the surface and a vertical cut within the same setup. The desired area for the cut was first evaporated with the process gas $(CH_3)_3CH_3C_5H_9$-Pt (trimethyl-methylcyclopentadienyl-platinum(IV)) by a built in gas injection system. After the organic part of the process gas had outgassed a platinum layer remained on the surface of the sample. It acted as a bonding agent in the following cutting process and as a contrast agent in the SEM image. The cut was then prepared in-situ using a 1 nA/30 kV gallium ion beam. Its length is about 3 μm and its depth is around 2 μm. A top view and a cut surface of the homogeneous area and the inhomogeneous area of the sample are shown in Figs. 2 and 3.

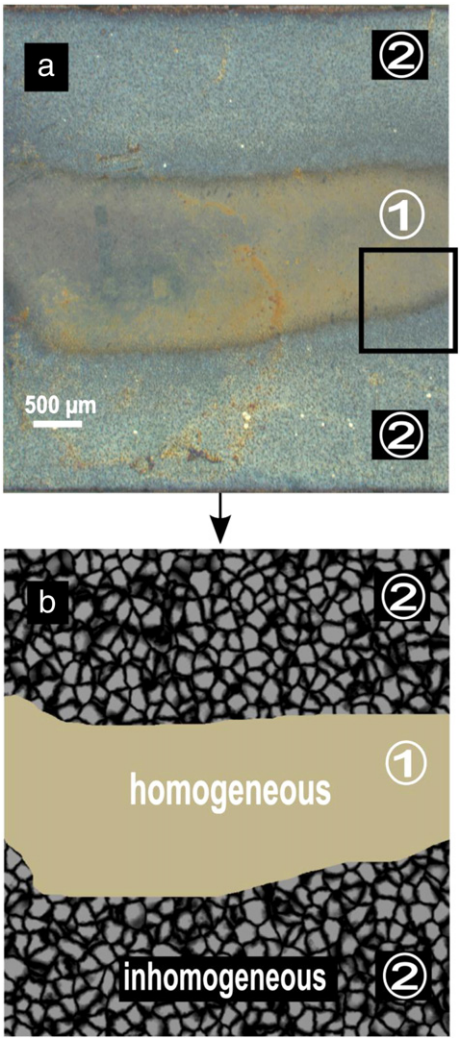


**Fig. 1.** Optical overview of a typical sample analyzed in this work. (a) The micrograph has been taken with an optical reflected-light microscope. (b) Sketch of homogeneous and inhomogeneous areas.

First we want to focus on the homogeneous inner area. Fig. 2(a) shows a SEM top view of this homogeneous area. The image shows an incomplete layer depicted in light gray, underneath a continuous layer in dark gray can be identified, which is the superconducting $MgB_2$ layer. The upper layer contains mainly Mg and shows holes of a typical size of several μm.

With a focused ion beam facility (FIB) a cut along the white solid line in Fig. 2(a) was performed to analyze the structure of the film. Fig. 2(b) shows a cross section of the film. From bottom to top four different regions can be recognized: the first layer is the substrate $Al_2O_3$ (light gray), the adjacent layer (dark gray, analog to Fig. 2(a)) is the $MgB_2$ layer. Black defect structures can be seen within this layer. They divide the $MgB_2$ layer into four sub-layers and originate from the four boron layers of the precursor. Covering the $MgB_2$ layer a third layer with a white flaky structure with some defects can be seen, which is Mg. The top layer is the platinum layer which was evaporated for preparation purposes of the cut. It was evaporated after Fig. 2(a) had been obtained.

Further characterization of the sample has been done using wavelength dispersive x-ray spectroscopy (WDX) which is installed in a *Cameca Sx 100* Electron Probe Micro Analyzer. The measurements were realized using an accelerating voltage of 15 kV, a beam current of 10 nA and a beam diameter of 5 μm. An overview of the obtained results for the dark layer and the light gray layer of the homogeneous part pictured in Fig. 2(a) is shown in Table 1. It has been found that the sample consists of around 65% boron and 35% magnesium at areas of the dark layer and of 31% boron and 69% magnesium at areas of the light gray layer. From the phase diagram [7,8] it can be concluded that the dark layer is the desired $MgB_2$ layer. The incomplete cover layer

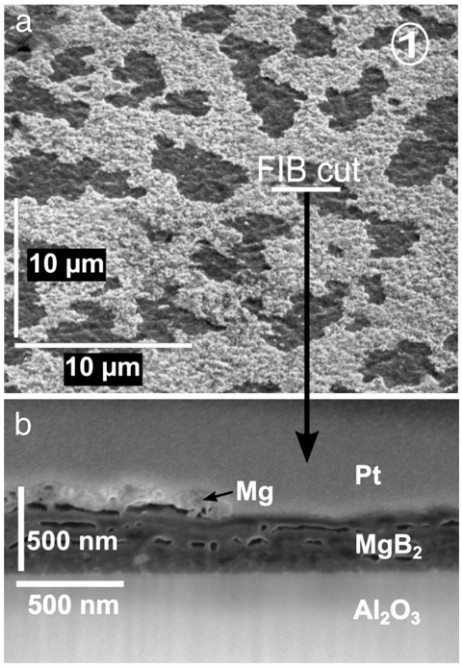


**Fig. 2.** Two images of the homogeneous area of a $MgB_2$ sample taken with SEM. (a) A top view under an angle of 52°. The dark layer consists of $MgB_2$ and is covered with an incomplete layer of Mg (light gray). The white line marks the location of the cut. (b) Cross section of the sample prepared by FIB. Pictured are from bottom to top: the substrate (light gray), the $MgB_2$ layer (dark gray) with defects (black), the incomplete layer of Mg (white) and the platinum layer (gray).