Reliable Preparation of High Quality Superconducting Thin MgB2 Films for Application

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Abstract. Since the discovery of its superconductivity [1], MgB2 attracts considerable attention. A number of groups have intensively tried to fabricate high-quality MgB2 films during the last years. However, the surface quality which is necessary for microelectronic device applications is still far from being achieved. In this work we report the growth and the properties of high-quality films which are prepared in a two-step process: 1) deposition of the precursor films and 2) their annealing in Mg vapor with a specially designed, reusable reactor [2]. The films were grown on single crystal substrates of R-cut Al2O3 as well as of Al2O3 (100), (1280 rot) LiNbO3 and MgO (100). The highest value of \(T_c\) = 39.4 K was observed for films deposited at 770 K on sapphire and MgO and annealed at 1120 K for one hour. Our method allows also the growth of high-\(T_c\) smooth films with high reproducibility and opens perspectives for the use of MgB2 films in microelectronics, especially for high-frequency applications.

1. Introduction
Since the discovery of its superconductivity,[1] magnesium diboride MgB2 has attracted increasing attention as far as its physical properties and the origin of its superconductivity are concerned. Magnesium diboride has a \(T_c\) (critical temperature) which is higher than that of conventional superconductors, a simple crystal structure, and a high coherence length in comparison to other metal-oxide high-\(T_c\) superconductors. The critical temperature of 39.3 K makes MgB2 an attractive candidate material for use in digital superconducting microelectronic devices operating at temperatures above 25
K, a temperature which is achievable in low-cost cryo coolers. For most of the microelectronic applications thin MgB$_2$ films with a high-quality crystal structure and a smooth surface would be needed. As an example one of the most successful and promising applications for MgB$_2$ is the preparation of DC-SQUIDs based on two SNS-junctions. These SQUIDs demonstrate a very low flux noise and magnetic field noise, which is 3 orders of magnitude lower than of YBCO-based SQUIDs, as low as 4 $\mu$Poisson Hz$^{-1/2}$ and 3.5 $10^{-14}$ THz$^{-1/2}$ at 19 K. In recent years many research groups have intensively tried to fabricate high-quality MgB$_2$ films. In this paper a reliable production method of making thin MgB$_2$ films with a high T$_c$ up to 39.4 K and smooth surfaces is presented and the products were studied in dependence of their production parameters with complementary analytical methods.

There are two main problems, making the preparation of MgB$_2$ films rather complex: the sensitivity of metallic Mg to oxidation during deposition and the large difference of the vapour pressures of B and Mg. The first problem can be solved by using an ultra-high-vacuum (UHV) chamber for the deposition of the pure metals B and Mg, or using a magnetron sputtering system with a high deposition rate. The second more complex problem is the high volatility against ambient of Mg, which leads to a deficiency of Mg in the films. As result of the intensive study up to now one can conclude, that there are three methods, which solve both of the above mentioned problems and allow the preparation of high quality MgB$_2$ films:

- “Two-step” synthesis with deposition of a precursor film (amorphous B or Mg-B composition films) as the first step, followed by annealing at high temperatures in Mg vapour in an evacuated container, as the second step. This technique has been quite successful in growing films with a high T$_c$, preferentially orientated grains and crystal structure. However, the surface quality is still insufficient for microelectronic device applications.

- “As-grown” synthesis – deposition in an UHV system of Mg and B from two sources on a substrate at low temperature (not higher than 350 °C, to avoid Mg losses) or the deposition of B in Mg vapour atmosphere.

- “One-step” The only purely in-situ “one-step” deposition process, which yields high-T$_c$ films has been reported by Zeng et al. using the HPCVD technique and the hazardous gas B$_2$H$_6$. However, it is not clear yet whether this method is also suitable for multilayer deposition.

DC magnetron sputtering is a simple and proper method for obtaining thin single layer or multilayer films with smooth surfaces and a highly orientated crystal structure. In the present work we report on the preparation of high-quality MgB$_2$ films on four different substrates, using an original technological “two-step” process of first sputtering of precursor films, which are as second step annealed in Mg vapour atmosphere in a special reusable Niobium (Nb) container.

2. Experimental

The deposition of the precursor film was performed in a vacuum system of the type of VUP-5 and AS400 with a self-designed DC magnetron. The diameter of the composite MgB$_2$-Mg target is 32 mm /68 mm. The technique of the target fabrication has been described already. After the deposition the precursor films and pure Mg powder were placed into the self sealing Nb reactor. The reactor is placed into a quartz tube which is pumped down to $10^{-6}$ mbar. The reactor is a Nb cylinder with a cavity for the placement of samples and Mg pieces. The conical shaped entry of the cylinder is closed by a water-cooled, conical Nb plunger, which is hermetically attached to the quartz tube before starting the reaction. The design of the constructed system possesses to maintain the necessary Mg vapour pressure while heating it up to 1000 °C. The container and the plunger can be easily separated mechanically after the annealing procedure. The temperature of the substrate during DC magnetron deposition was varied from 20 °C up to 600 °C. Post-annealing in the Nb reactor was carried out at several temperatures from 800 °C to 900 °C and at several annealing times from 30 min to 90 min. The presence of condensed Mg on the inner part of the plunger surface after annealing is the evidence of a sufficient concentration of Mg vapour during annealing. The films were grown on single crystal substrates of Al$_2$O$_3$(1102) as well as of Al$_2$O$_3$ (100), MgO (100) generally used for MgB$_2$ film.
fabrication [21] and (128° rot) LiNbO3 with a trigonal crystal structure the latter not matching to the 
MgB2 structure.

The MgB2 films were studied by X-ray diffraction techniques (DRON-2.0 from Rigaku company and Xpert pro Systems from Phillips, with CuKα radiation), Atomic Force Microscopy (AFM) and Scanning Auger Electron Spectrometry (SAES). Typical dimensions of the samples were 10 mm in length and 5 mm or 10 mm in width. The thickness of the films varied from 150 nm to about 1 µm. For some of the rough, dull films the thickness varied up to a maximum thickness of 6 µm. Resistivity was measured by a standard DC four-probe method with sealed contacts.

For AFM measurements a modified commercial system from Nanoscope (Multimode) and a commercial system from NT/MDT (Solver) were used in the Contact Mode and Intermittent Contact Mode. The AFM data was analysed with SPIP Software. SAES including both surface analysis and depth profiling was made with a “Phi680 Auger Nanoprobe” system from PHI company, with about 15 nm lateral resolution.

Figure 1: Comparison of superconductivity and structure of MgB2 films surfaces. (1) Resistive characteristics and superconducting transition (inset) for films deposited at 500 ºC (b, “dull”) and without heating (a, “mirror”) on sapphire (100). (2) X-ray diffraction pattern of the MgB2 film on MgO (100). (a) mirror sample, (b) dull sample, inset: part diffraction pattern in the angle range of 41° - 44°.

3. Results and Discussion

The MgB2 films which were deposited on Al2O3 (1102), Al2O3 (100) and MgO (100) substrates under the same technological conditions showed identical morphology and best superconducting properties (see Fig 1.1). The films on LiNbO3 substrates were deposited even without heating and have slightly poorer superconducting properties 

| Ts (ºC) | R300/R40 | Tc (K) | ΔTc (K) |
|---------|----------|--------|---------|
| <100 ºC | 1.37     | 36.3   | 0.2     |
| 400     | 1.8      | 36.5   | 0.5     |
| 450     | 1.7      | 36.1   | 1       |
| 500     | 2.8      | 39.4   | 0.3     |
| 600     | 1.45     | 33.7   | 1.6     |

Thus we can agree with [21] that the substrate mismatch is not crucial for superconducting properties of sufficiently thick (≥ 100 nm) MgB2 films.

The critical temperature and the width of transition of the films prepared on Al2O3 and
MgO substrates are close to $T_c$ for MgB$_2$ bulk material. It was found (Tab. 1) that during the deposition of the precursor films the temperature regime plays a crucial role for the quality of the samples. The best $T_c$ (39.4 K) was observed for films which were deposited at 500 °C and have high surface corrugations (eg. sample b), whereas the smoother surfaces and the more preferable c orientations were observed in films deposited at low temperatures (eg. sample a).

The resistive characteristics and the temperature of superconducting transition are presented in Fig. 1.1. The results of the X-ray diffraction analysis for the films deposited on MgO substrate which were fabricated in these two different temperature regimes are presented in Fig. 1.2. The diffraction patterns show the presence of both MgB$_2$ and MgO. The parameters of the MgB$_2$ unit cell are $a = 3.08$ Å, $c = 3.53$ Å, which are close to the values for a and c of bulk MgB$_2$. Additional phases are absent. The widths of different reflections are different (Tab.2).

For (00l) reflections typical widths are smaller than for the (kh0) reflection. The size of the grains is bigger than 500 Å in <001> direction and about 100 Å in <100> direction (for sample (b)), bigger than 500 Å in <001> direction and about 250 Å in <100> direction (for sample (a)). The quantity of MgO in the sample (a) is more (about 50%) than in the sample (b) (less than 30%). The X-ray diffraction analysis shows almost the same data for the films on sapphire substrates.

The AFM images shown in Fig. 2.1 and Fig. 2.2 give important information about the surface structure of the films. The surface roughness of the films prepared with the “two-step” process of DC magnetron sputtering and annealing in Mg atmosphere changes significantly with the temperature of the substrate. The film sample a in Fig 2.1 demonstrates a smooth surface with an average roughness (RMS) of about 8 nm and below. It also exhibits the preferable c orientation. The randomly orientated film sample b in Fig. 2.2 has a high roughness ranging from about 100 nm up to the micron range.

![AFM images](1) (2)

**Figure 2:** AFM analysis of a smooth (“mirror”) and a rough (“dull”) sample. (1) AFM image of the surface of a smooth film, a 400 nm thick layer of MgB$_2$ on (100) sapphire ($T_{\text{substrate}} <200$ °C, $T_c = 39.3$ K) obtained in the intermittent contact mode; scan size: 2.5 µm x 2.5 µm; z-scale: 30 nm, RMS surface roughness value: 8.5 nm +/-1.3 nm, average island size 50 nm. (2) AFM image of the surface of a 1100 nm thick “dull” film of MgB$_2$ on (100) sapphire ($T_{\text{substrate}} = 500$ °C; $T_c = 39.3$ K) obtained in the Contact Mode; scan size: 4.2 µm x 4.2 µm; z scale: 5 µm; RMS = 302 nm.

In both cases, no topography-independent material contrast is found in the friction and phase information of the AFM measurements. This means that the surfaces mainly consist of one
homogeneous material independent of the temperature treatment of the films. A higher contamination with MgO lowers $T_c$ (Fig. 1.1) and reduces the ratio of the value for $R_{300}/R_{40}$, while the width of the superconducting transition for the films deposited at 500 °C and without heating below 100 °C is about equal.

Figure 3: (1) SAES analysis of one “mirror”-like film on Al$_2$O$_3$ substrate; the virtual depth of the layer is 580 nm. The signal for oxygen close to the substrate surface could partly result from a reaction with the Al$_2$O$_3$ substrate; (2) SAES analysis of one “dull” film; the virtual depth of the layer 1.1 µm; Oxygen signal results from a native oxide layer at the surface of the MgB$_2$ film. The signal for the Al element and O element is naturally rising at the substrate film border.

The SAES (Scanning Auger Electron Spectrometry) depth profile analysis of sample a (Fig. 1.1), as an example of mirror-like films, is shown in Fig. 3.1 reveals the presence of some oxide contaminations in two regions, one near the surface and one near the substrate. Both regions show a similar thickness of about 100 nm. The possible reason for the contamination at the surface is normal oxidation of the material under ambient conditions, which always generates oxide-containing regions of this thickness (depending on the average island size of 50 nm) within a short time. Even long-term oxidation experiments under ambient conditions show about the same thickness for oxide contamination that is found after half an hour in an ambient atmosphere. Freshly prepared MgB$_2$ layers hardly exhibit any oxygen contamination at the surface. The oxygen contamination near the substrate may be a result of an interface reaction with the substrate during the heating periods at elevated temperatures.

Table 3.1: The influence of annealing time on the $T_c$, resistance broadening $\Delta T_c$ and $R_{300}/R_{40}$ for MgB$_2$ films on sapphire with a thickness of 1 µm prepared at annealing temperature of 850 °C.

| Annealing time (min) | $R_{300}/R_{40}$ | $T_c$ (K) | $\Delta T_c$ (K) |
|---------------------|------------------|-----------|------------------|
| 30                  | 1.4              | 34        | 2.5              |
| 60                  | 2.8              | 39.4      | 0.3              |
| 90                  | 2                | 37.6      | 0.4              |

As an example for the SAES analysis of the dull films the depth profile of sample b (Fig. 1.1) is shown in Fig. 3.2, which demonstrates that also rough MgB$_2$ films have a stoichiometric order and a clean composition of MgB$_2$. Of course, there is no such sharp border between the signals from the film and the signals from the substrate as in the case of the smooth layers, which is due to the high surface roughness. The influences of the annealing time and annealing temperature on the quality of the prepared films on sapphire substrates are presented in Tab. 3.1 and Tab. 3.2. Obviously, the optimal
The temperature regime for annealing MgB$_2$ films is at about 850 °C and the optimum time for annealing is about 60 min.

### Table 3.2: The influence of annealing temperature on the $T_c$, resistance broadening $\Delta T_c$ and R300/R40 for MgB$_2$ films on sapphire with a thickness of 1 µm prepared with an annealing period of 60 min.

| Annealing temperature (°C) | R300/R40 | $T_c$ (K) | $\Delta T_c$ (K) |
|----------------------------|----------|----------|------------------|
| 800                        | 1.5      | 34       | 2.1              |
| 850                        | 2.8      | 39.4     | 0.3              |
| 900                        | 1.9      | 35.6     | 1.7              |

4. Conclusion

To conclude we have reported about the growth of textured, smooth and rough MgB$_2$ films on different substrates. Annealing inside a self-sealing reusable Nb reactor allows a quite reliable, reproducible fabrication of high-quality MgB$_2$ films. The growth of smooth high-$T_c$ (39.4 K) films with a simple method of reliable reproducibility opens up perspectives for the use of MgB$_2$ films in microelectronics, especially for high-frequency applications. The best results of films with smooth surfaces and good c-orientation having at the same time high $T_c$ were obtained by a novel “two step” synthesis path on Sapphire and MgO surfaces with and without annealing during Sputtering and second step annealing at 1120 K for about 60 minutes. Lithium Niobate as substrate in any case or with the other substrates the annealing of the samples during the sputtering of the precursors leads to rough sample surfaces.

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