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High-quality MgB_2 thin films *in situ* grown by dc magnetron sputtering

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Abstract
Thin films of the recently discovered magnesium diboride (MgB_2) intermetallic superconducting compound have been grown using a magnetron sputtering deposition technique followed by *in situ* annealing at 830 °C. High-quality films were obtained on both sapphire and MgO substrates. The best films showed a maximum T_c of 35 K (onset), a transition width of 0.5 K, a residual resisitivity ratio up to 1.6, a low-temperature critical current density $J_c > 10^6$ A cm^{-2} and an anisotropic critical field with $\gamma \cong 2.5$ close to the values obtained for single crystals. The preparation technique can be easily scaled to produce large-area *in situ* films.

1. Introduction

The recently discovered intermetallic superconducting compound MgB_2 [1] presents very interesting aspects related to its record T_c for non-oxide inorganic superconductors (40 K), to its anisotropic superconducting properties and to its intriguing two-band electronic structure [2].

Thin films of MgB_2 are of special interest for microelectronic devices due to the relatively high T_c, the sufficiently long coherence length and the fairly high critical current density [3–5]. The availability of *in situ* deposited, large-area high-quality films using relatively simple techniques is of great importance for the development of such applications. Unfortunately, the high vapour pressure of Mg even at low temperatures has made it difficult to realize high-quality thin films in a single step, without a Mg high-pressure post-anneal [6–8], which is extremely desirable for a large number of studies and applications.

As a second possibility, two-step *in situ* processes can be of interest in the same framework. Many groups have realized reasonable quality *in situ* films by pulsed laser deposition (PLD) techniques and a subsequent high-temperature annealing procedure [9–11], or by a single step procedure [12, 13]. The results were encouraging though the resulting film quality was inferior in comparison with the best films obtained using *ex situ* annealing treatments at much higher Mg partial pressures [6–13]. To our knowledge, the only MgB_2 thin films obtained without *ex situ* annealing with $T_c > 30$ K are those reported in [11] (*in situ* annealed) and [13] (as-grown). Furthermore, up to now, there have only been a few reports in the literature about MgB_2 thin-film deposition by sputtering [14, 15].

In this paper, we present a simple, innovative method to produce high-quality films by a two-step, *in situ* technique starting with a precursor film obtained by magnetron sputtering. Among other advantages, the proposed procedure can be easily scaled to obtain large-area films for practical applications.

2. Fabrication procedure and structural characterization

MgB_2 thin films were grown at INFM, University of Naples, by a planar magnetron sputtering technique in an ultra-high vacuum (UHV) system operating at a base pressure in the low 10^{-7} Pa range. The design, construction and testing of the balanced magnetron unit used have been reported in [16]. In brief, the system is equipped with three focused 2 inch magnetron sources. The substrates (sapphire or MgO) are placed 'on-axis' at variable distances from the target well outside the plasma region.

During the deposition of the precursor film the substrates were placed over a thin Mg disc, on the bottom of a cylindrical Nb box ($h = 4$ mm) placed on the surface of a molybdenum heater. The precursor deposition was performed at room temperature. Only a minor increase of the substrate temperature (up to 60 °C) was observed during deposition.

After the deposition, using tweezers mounted on a wobble stick, the Nb box is well closed by a properly designed cap. An indium wire gasket is inserted between the box and the cap. At this point the heater is switched on and ramped up to the desired temperature. The indium gasket melting guarantees a perfect sealing of the box. The box design and the internal Mg

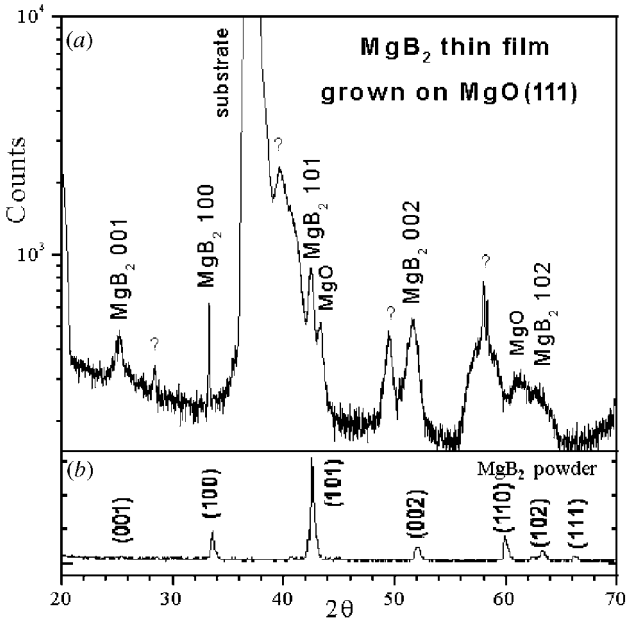

Figure 1. (*a*) XRD (θ–2θ) spectrum for a MgB_2 film on a MgO (111) substrate. (*b*) Comparison with a θ–2θ spectrum obtained on MgB_2 powders (from [6]).

overpressure (due to the presence of the Mg disc) prevent any In diffusion in the film. The process is therefore conducted in saturated Mg vapour as in *ex situ* processes, giving a high level of film quality and reproducibility.

The best results were obtained by co-depositing MgB_2 and Mg for 10 min on R-cut sapphire, resulting in a Mg-rich Mg–B precursor film. The target voltages and current were 460 V (MgB_2 target), 400 V (Mg target) and 1 A respectively. The argon pressure during sputtering was 9×10^{-1} Pa. However, this seems not to be critical and films with similar properties were made starting from precursors obtained by sputtering only from the MgB_2 target. No attempts have been made at present to start from B or B-rich Mg–B precursors.

Typical post-annealing processes were carried out at a substrate temperature $T_s = 830$ °C for 10 min (about 30 min were required to reach the equilibrium temperature). After deposition, the films can be removed from the system in the sealed Nb box for transfer into a UHV environment for surface studies (scanning tunnelling microscopy or others). The box can also be easily opened *in situ* with a properly designed device for further film processing (junction fabrication or other uses). The process is highly reproducible and similar results were obtained on both sapphire and MgO substrates. Depending on deposition time and precursor composition, the film thickness, measured with a standard stylus profilometer, was in the range of 0.8–1.0 μm.

The x-ray diffraction (XRD) pattern (Cu Kα), shown in figure 1 for a film deposited on crystalline MgO(111), shows the MgB_2 phase with small amounts of MgO (due to the oxidation of excess Mg) and some unidentified spurious phases. By comparing the experimental spectra with those obtained on powders, the relative height of the peaks indicates a wide *c*-axis orientation of our films. From peaks positions, we can estimate the lattice parameters: $a = b = 0.310 \pm 0.002$ nm, $c = 0.353 \pm 0.005$ nm. The x-rays of optimized films on R-cut sapphire are not reported because of the overlap of the (00*n*) film reflections with the Al_2O_3 substrate reflections.

The film surface morphology was investigated by atomic force microscopy (AFM), showing a granular nature of the films. The roughness on a single grain (columnar nature, a few micrometres wide) is about 50 nm.

3. Main normal state and superconducting properties

Figure 2 shows the resistivity as a function of temperature for a typical film grown on a sapphire substrate in the standard conditions described in the previous section. The absolute value of resistivity was determined using a commercial linear four-probe station, the main error being associated with the effective thickness overestimation due to the strong granular nature of the samples with a small contact area between the grains. The estimated room-temperature resistivity is about 200 $\mu\Omega$ cm, much higher than in single crystals. However, this value should only be considered as an upper limit. Similar or higher values have been reported in the literature for films [3, 5], possibly due to similar effective thickness problems and/or to oxygen contamination [3]. We cannot exclude oxygen contamination in our films either (possibly coming from the target). In any case, we do not have any definite explanation for the reduced maximum onset critical temperature of our films (35 K).

The transition width is $\Delta T_c = 0.5$ K (10–90% criterion). Equivalent results were obtained for films grown on MgO substrates. In the temperature range explored, the resisitivity closely follows a Bloch–Gruneisen law. The full curve in figure 2 represents the best fit of the data. From the best-fit procedure, we obtained a Debye temperature $\Theta_D = 1100 \pm 50$ K. This value is higher than that generally reported from specific heat measurements [5] but comparable with other estimates from resistivity measurements [17]. At low temperatures, a clear T^3 dependence is observed as generally reported in the literature [5].

Our best films had a residual resistivity ratio (RRR) $\beta = \rho$ (300 K)/ρ (40 K) = 1.6. A clear T_c–β correlation has been observed in films of different quality, as shown in the inset of figure 2. The observed relation strongly resembles the behaviour of many intermetallic classic superconducting compounds (Nb, A15) [5] as well as borocarbides [18]. The best films exhibit a transport critical current density up to 2.5 MA cm^{-2} at 11 K. This is discussed elsewhere [19].

The values of T_c and J_c of our films were also evaluated inductively by measuring the third-harmonic component voltage U_3 across a small sensor coil mounted very close to the film surface, as a function of temperature or driving current, respectively [20]. The temperature dependence of the critical current performed by this method on one of our films (Al_2O_3 substrate, $T_c = 30$ K) is shown in figure 3. The extrapolated value for the zero-field, zero-temperature critical current is $J_c(0) = 1.6$ MA cm^{-2} (see figure 1). In the inset, the T_c evaluation using a plot of U_3 versus T is also shown (as generally observed by this method, the onset of the U_3 signal roughly corresponds to the zero resistance value temperature in resistive measurements).

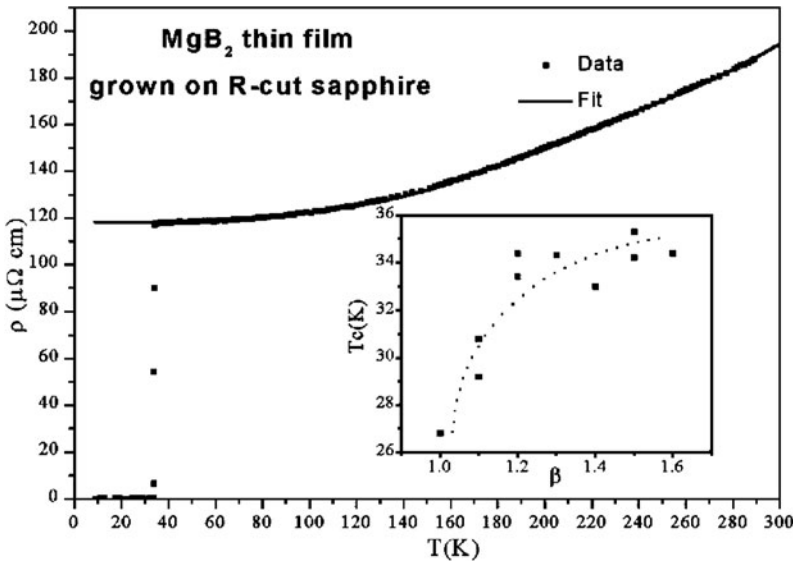

Figure 2. Resistivity versus temperature for a MgB_2 film grown on R-cut Al_2O_3 substrate. The full curve represents the fit made using the generalized Bloch–Gruneisen formula. The inset shows the correlation between the residual resistivity ratio (β) and T_c.

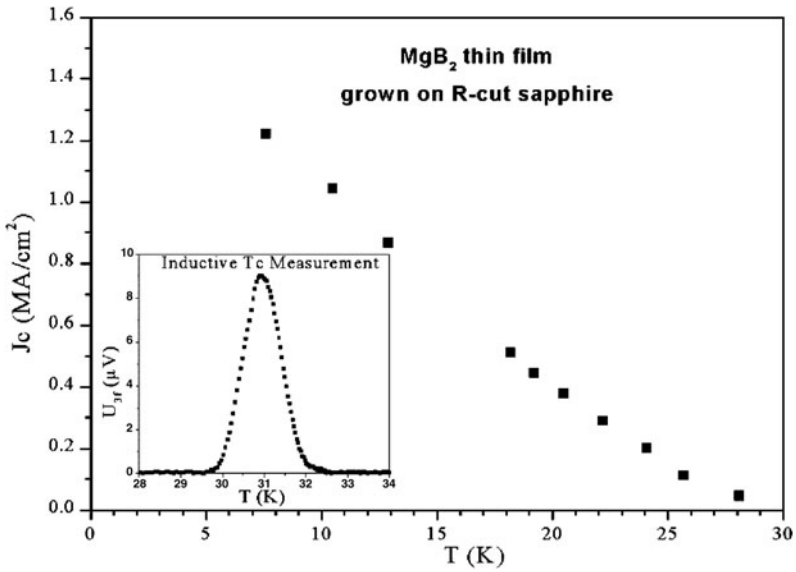

Figure 3. Critical current density versus temperature for a MgB_2 film grown on an Al_2O_3 substrate. The inset shows an inductive measurement of T_c.

Table 1. The main properties of our best films.

T_c (K)	ΔT_c (K)	β	ρ ($\mu\Omega$ cm)	J_c (MA cm^{-2}, 0 field)	$H_{c2\ par}$ (T) at $T = 25.7$ K	$H_{c2\ perp}$ (T) at $T = 25.7$ K	Thickness (μm)	Substrate
35	0.5	1.6	200	2 (at 11 K)	8.0	2.9	0.8–1.0	MgO, Al_2O_3

Figure 4 shows the temperature dependence of the upper critical field, in both parallel and perpendicular directions with respect to the film plane, up to a maximum field of 8 tesla for one of our films (Al_2O_3 substrate, $T_c = 35$ K). As typically reported [5], both curves show a slight upward curvature close to T_c. From the critical field slope we can estimate [21, 22], at $T = 0$ K, $\xi_\perp = 2.3 \pm 0.1$ nm and $\xi_{||} = 5.7 \pm 0.2$ nm and an anisotropy ratio $\gamma = 2.5$ (slowly temperature-dependent). This value agrees fairly well with some current determinations on single crystals [23, 24], indirectly proving the high-quality and c-axis orientation of our films. It is worth pointing out that the film on the MgO substrate shown in figure 1 ($T_c = 32$ K) showed a lower anisotropy ($\gamma = 1.4$), corresponding to the partial c-axis orientation. Although we do not have direct proof, we assume that films on Al_2O_3 are indeed fully c-axis oriented. A perfect fitting of the angular dependence of the critical field with the Ginzburg–Landau formula [25] was possible at all temperatures. Non-optimized films presented a

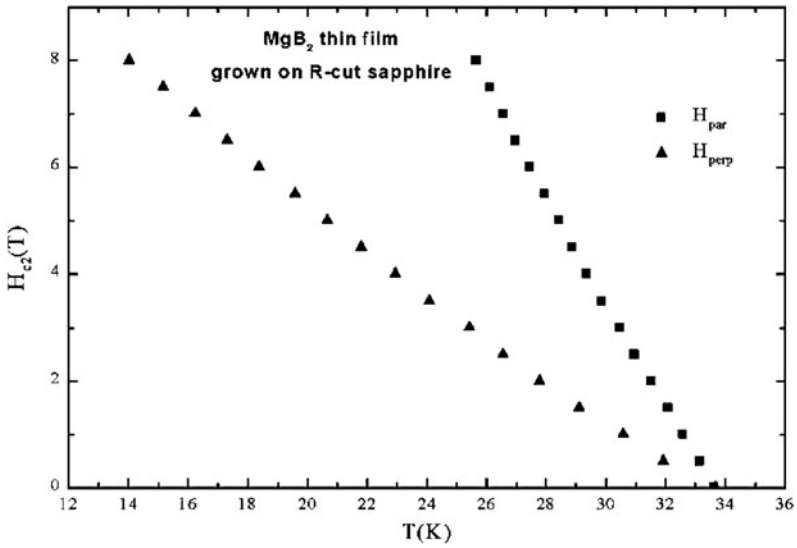

Figure 4. Temperature dependence of the upper critical field in both parallel and perpendicular directions with respect to the film plane for a MgB_2 film grown on an Al_2O_3 substrate.

somewhat lower γ. Full critical field anisotropy measurements and analysis, as well as critical current measurements versus magnetic field, are reported elsewhere [19].

Finally, in table 1 the main properties of our films are summarized. These compare well with the best films obtained up to now [14].

4. Conclusion

In conclusion, we have presented a new method to produce high-quality films using a two-step *in situ* technique starting with a precursor film obtained by magnetron sputtering. The fabrication process still has to be fully optimized but the overall film quality compares well to the best films obtained by two-step *ex situ* processes. The proposed preparation technique can be easily scaled to produce large-area *in situ* films for different applications.

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