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FLUX PINNING IN MgB_2 THIN FILMS GROWN BY PULSED LASER DEPOSITION

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A number of *c*-axis oriented MgB_2 thin films were grown *in-situ* by pulsed laser deposition (PLD) on Al_2O_3-R cut, and the pinning properties were investigated using transport, DC magnetisation and magneto-optical imaging (MOI) techniques. It was found that at temperatures below 10K and large applied DC magnetic fields, the irreversibility line of *in-situ* MgB_2 thin films is higher that a bulk material. The critical current density J_c of *in-situ* thin films is less dependent on the applied magnetic field B than the current density J_c of an *ex-situ* MgB_2 film or bulk. The penetration of magnetic field inside the film is uniform, and it follows the theoretical prediction for a homogenous thin film.

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1. Introduction

The discovery of superconductivity in MgB_2 with a transition temperature T_c = 39 K [1], opens the possibility of replacing Nb_3Sn (T_c = 18 K) or Nb_3Ge (T_c = 23 K) used in superconducting magnets and electronic devices. In addition to a higher operating temperature, other advantages offered by this new superconductor are a simple structure, large coherence length (ξ~5 nm) [2] and large critical currents in high magnetic fields [3].

The MgB_2 material is known already for some time [4]. It has a hexagonal AlB_2-type structure indexed in the space group *P6/mmm*, with B layers separated by Mg. Initially it was prepared in bulk form, and only recently in the form of wires, thin films and single crystals. For device applications, as well as for investigation of other superconducting properties, it is desirable to have epitaxial thin films. In particular high quality multi-layer epitaxial films are highly desirable for devices.

The main difficulties in growing high-quality MgB_2 films are the large difference in vapour pressure between magnesium and boron, and the high reactivity of magnesium with oxygen. For the PLD method, which is inherently a non-equilibrium process, the problem posed by the large difference in vapour pressure between magnesium and boron is difficult to overcome. The high reactivity of magnesium with oxygen can be overcome by reducing the amount of oxygen present in the deposition atmosphere.

In general, for MgB_2 thin films growth, two successful methods have been used so far. Encouraging results on various substrates were obtained for: a) a two-step procedure, which consists of B deposition followed by *ex-situ* Mg diffusion [5,6] and b) a single-step procedure, which consists of Mg and B deposition *in-situ* [7,8]. The best results reported so far in terms of T_c and J_c have been achieved using the two-step procedure.

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So far all MgB_2 films grown by a single-step procedure were not epitaxial. Evidence of epitaxial growths was reported only for the two-step procedure, using RF sputtering of boron and post-deposition annealing in magnesium vapours at 850 ºC [9]. However, from the devices point of view, the second fabrication method is more attractive for it is the only one capable to produce thin films with a multi-layer architecture. It is therefore desirable to improve the quality of MgB_2 films produced in-situ.

In this report we present results on the pinning properties of MgB_2 thin films grown *in-situ* by PLD, which include the effect of the deposition atmosphere and laser fluence on the stoichiometry of MgB_2 films.

2. Experimental

The MgB_2 thin films used in this work were produced using a standard PLD system. The PLD system comprises a UV excimer laser (λ = 248 nm, pulse duration 25 ns); a fixed-beam optical train that focus the beam on a rotating target; a vacuum chamber with a base pressure of 1×10^{-7} Torr (7.5×10^{-10} Pa).

The depositions of MgB_2 thin films were carried out on Al_2O_3-R, using two main routes. The first route (*in-situ)* started with a 5 min deposition from a stoichiometric MgB_2 target at a substrate temperature of 250 ºC, and a 3 min deposition of a Mg cap layer from a Mg target, at the same temperature, at 130 mTorr (17.3 Pa) of high-purity Ar. This was followed by *in-situ* annealing at 680 ºC for 10 min, at a pressure of 763 Torr of high-purity Ar. The MgB_2 film thickness obtained with this procedure was ~600 nm. The second route (*ex-situ*) started with a 10 min deposition from a B target, at a substrate temperature of 250 ºC and 130 mTorr of high-purity Ar, followed by *ex-situ* annealing at 900 ºC, in Mg vapours for 30 min. The MgB_2 film thickness obtained with this procedure was also ~600 nm. For al depositions, the optimum laser fluence was ~2.3 J/cm^2, the repetition rate was 10 Hz, and the target-substrate distance was 25 mm.

As the Mg vapours are highly susceptible to oxidation, the level of oxygen in the chamber during the deposition process has to be strictly controlled. Possible sources of oxygen are the atmosphere of the chamber and the target. The first source can be greatly reduced by standard vacuum deposition procedures, such as low pressure, baking, flushing with dry gas, etc. The target may contribute to the level of oxygen in the deposition chamber mainly because of its porosity. It is particularly important to minimise this source of Mg oxidation since it is a very effective one. In our experiments we used a stoichiometric MgB_2 target having a density of 84% of the theoretical (X-ray) density, which was produced by hot isostatic pressing (HIP). An increase of target density above 84% was unsuccessfully attempted.

The optimisation of deposition conditions for the *in-situ* deposition route was carried out on three sets of films, produced at room temperature, at different laser fluences: ~1.3 J/cm^2; ~1.8 J/cm^2; and ~2.3 J/cm^2. Each set contained five films, produced at different background pressures of high-purity Ar: 1 mTorr (0.133 Pa); 50 mTorr (6.65 Pa); 100 mTorr (13.3 Pa); 150 mTorr (19.95 Pa); and 200 mTorr (26.6 Pa).

The relative concentration of Mg and B of each film was measured by inductive coupled plasma spectroscopy (ICP), using a Varian Vista MPX axial spectrometer. The phase composition of targets and films was investigated by X-ray diffraction in θ-2θ geometry, using a MAC Science three-independent axes diffractometer. Normal-to-superconducting transition temperatures T_c for the films were obtain by DC magnetization, on a SQUID magnetometer (Quantum Design MPMS system). The magnetic critical current density J_c was calculated using an extended Bean's model, from dc-magnetisation measurements up to an applied field of 5T, measured at different temperatures, using the same system mentioned above. Transport measurements were carried out using 4-probe technique at DC fields up to 9T, applied perpendicular to the (a,b) plane of the film. A Quantum Design PPMS system was used for this purpose. The local magnetisation behaviour of the optimally produced films was investigated by magneto-optic imaging (MOI), and compared with the theoretical predictions.

3. Results and discussion

In addition to the need for the chemical potential, the occurrence of the process of the stoichiometric condensation of MgB_2 films requires that both Mg and B have certain energy levels. For a fixed laser spot geometry, and target-substrate distance, these energy levels are controlled by laser fluence, and deposition pressure with opposite effects.

The variation of the relative concentration of Mg present on the substrate was measured by ICP, and presented in Fig. 1 as a function of laser fluence *E* and deposition pressure *p*. In this experiment we used three laser fluences (~1.3 J/cm^2; ~1.8 J/cm^2; ~2.3 J/cm^2), and five deposition pressures (1 mTorr; 50 mTorr; 100 mTorr; 150 mTorr; 200 mTorr) of high purity Ar.

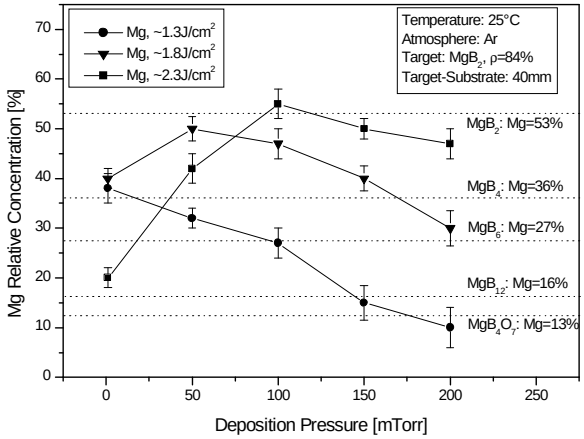

Fig. 1. Relative concentration of Mg on the substrate measured by ICP, and presented as a function of deposition pressure and laser fluence.

At the lowest fluence of ~1.3 J/cm^2, the relative concentration of Mg, measured on the substrate decreases continuously with the increase of the deposition pressure. On the same figure are represented the lines of constant Mg concentration in the main phases present in Mg-B-O system, which are close to MgB_2 in terms of Mg concentration.

The result shows that at the lowest fluence, the highest relative concentration of Mg measured on the substrate is ~40% Mg. At this relative concentration, MgB_2 phase cannot be formed, since the stoichiometric MgB_2 contains 53% of Mg. In this case, other phases with a lesser Mg proportion are more likely to be formed, such as MgB_4. At a higher laser fluence of ~1.8 J/cm^2, the relative concentration of Mg measured on the substrate is reaching a maximum of ~50% Mg, at a deposition pressure of ~50 mTorr.

This result shows that for lower deposition pressures, Mg has a too high energy in order to be retained on the substrate and form MgB_2. On the other hand, for higher deposition pressures, the slowing down of Mg due to an increased number of collisions becomes predominant. As the result, the relative concentration of Mg on the substrate is decreasing, and again, the formation of MgB_2 film is less likely to take place.

At the highest fluence of ~2.3 J/cm^2, a similar dependence of the relative concentration of Mg versus the deposition pressure occurs. In this case however, the maximum is at ~55% Mg, at a deposition pressure of ~100 mTorr, and the relative concentration of Mg and B on the substrate allows the formation of MgB_2 film in-situ. These results are consistent with a recent spectroscopic investigation of the MgB_2 plasma dynamics in Ar atmosphere [10], which showed that for a background pressure higher than ~1.5 mTorr, the time-of-flight distribution of Mg I emission line (383 nm), measured at a distance of 5 mm from the target, is continuous, indicating the onset of a slowing down effect of the Ar atmosphere.

These optimum conditions were used in the process of fabrication the MgB_2 films, as illustrated in Fig. 1, using a laser fluence of ~2.3 J/cm^2 and a background pressure of high purity Ar,

of 130 mTorr. In addition, a repetition rate of 10 Hz and a deposition time of 10 min were used. After the deposition, a cap layer of pure Mg was deposited from a separate target, and the film was annealed *in-situ* at 680 ºC for 10 min.

A second MgB_2 film was produced using an *ex-situ* procedure, which consisted of depositing a B film, approximately 600 nm thick, encapsulating the film in a pure Fe container, together with Mg powder, under an atmosphere of high purity Ar, and annealing the container at 900 ºC for 30 min. The encapsulation was carried out as follows: the B film and the Mg powder were placed inside a Fe tube with one end closed; the procedure took place in a glovebox filled with high-purity Ar; the open end of the Fe tube was sealed with a valve, taken outside the glovebox; the Fe tube was sealed by pressing.

The X-ray orientation of the MgB_2 films is difficult to observe. Both, out-of-plane and in-plane signals are weak due to the small crystal size produced in the films. However, it can be said that the films are c-axis oriented. The in-plane orientation of the films should be attributed to the type of substrate used in this experiments. Indeed, Al_2O_3 has a hexagonal structure (R-3cH), but the Al_2O_3-R cut substrate has a rectangular surface lattice, with the surface lattice constants a = 4.76 Å and b = 15.38 Å. A favourable (00l) orientation of the hexagonal MgB_2 film on such a surface could produce the following orientation relationship between the substrate and the film: $[1\bar{1}2]$ Al_2O_3 || $[1\bar{1}0]$ MgB_2. This would result in a lattice mismatch of ~4% along $[1\bar{1}2]$ Al_2O_3 and ~35% along $[1\bar{1}0]$ Al_2O_3 directions. For such an orientation relationship, the film should have a 60º in-plane rotation relative to the substrate.

Previous research [11] suggested that the necessary conditions for epitaxial growth are a two-dimensional superlattice cell area of less than 60 nm^2, and a lattice mismatch at the interface between the two-dimensional superlattice cells of less than 1%. These conditions had been verified experimentally on other film/substrate systems [12].

In the case of MgB_2/Al_2O_3-R, the above conditions are not satisfied, and this could explain why the in-plane orientation of the film is poor. In the case of MgB_2/(001)SiC the epitaxial growth condition mentioned above is satisfied [13]. So far there is only one report on MgB_2 film grown on SiC, but the transition temperature reported was low, at an onset of ~25 K, and the orientation of the film was not indicated [14].

The normal-to-superconducting transition temperature of the films produced *in-situ* was measured by the 4-probe method, in applied DC fields up to 9T, applied perpendicular to the substrate surface (parallel to the c-axis of the film). The results are presented in Fig. 2, and display weak field dependence. The inset of the figure shows the resistance versus temperature dependence in the range from room temperature to 5 K, at zero applied DC field. A residual resistance ratio (RRR) [RRR=R(300 K)/R(40 K)] of 1.08 was obtained. This value is much smaller than the RRR for bulk MgB_2, for which it can have values from 2 (our sample) to 20 [15], and even smaller than bulk MgB_2 doped with SiC, for which RRR is that of 1.74 [16]. This suggests that the pinning of the *in-situ* grown film is stronger than the bulk MgB_2.

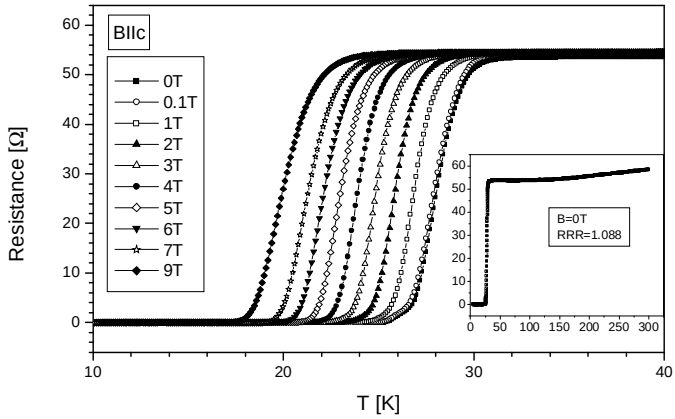

Fig. 2. Resistive transition in applied DC fields up to 9T for MgB_2 film grown in-situ by PLD. The inset shows the R-T curve at zero applied field for the same sample from 300 K down to 5 K.

The higher critical field $H_{c2}^{\parallel}$ dependence on temperature, extracted from R(T, B) curves is presented in Fig. 3, together with the irreversibility line of bulk MgB_2 derived in the same way. It is evident that for temperatures below 20 K, the flux pinning for the in-situ film is stronger than in the bulk, in spite of the fact that the onset of superconducting transition in the film was 30 K, and in the bulk was 39 K.

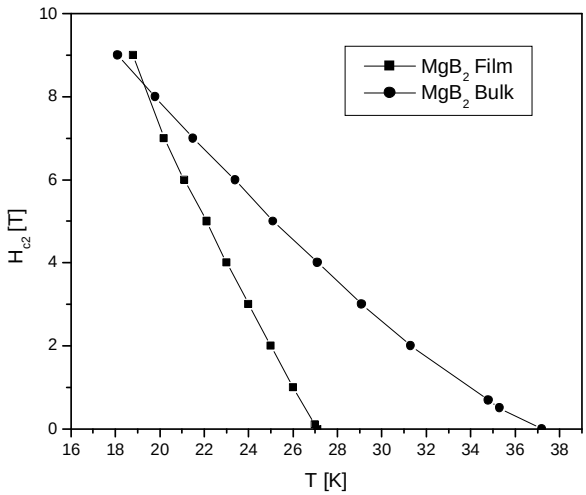

Fig. 3. Higher critical field (H_{c2}) versus temperature for MgB_2 thin film grown *in-situ* by PLD, and for MgB_2 bulk.

The decrease in T_c between the bulk and thin film may be attributed to the influence, which a lower degree of crystalinity can have on the phonon spectrum of the MgB_2 crystal lattice [17].

The dynamics of magnetic flux penetration in MgB_2 film grown in-situ was investigated using MOI technique [18], using Fe-garnet as indicator film, deposited by magnetron sputtering. The DC probe field was 50 mT, applied parallel to the c-axis of the film, and the result at 20 K is presented in Fig. 4, where the bright square represent the location of the edges of the substrate.

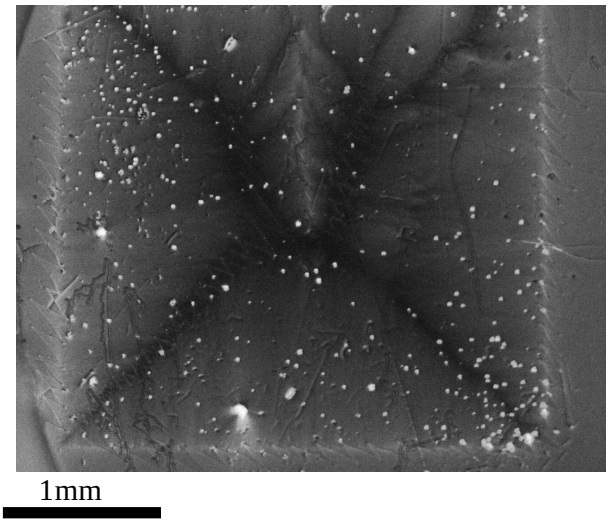

Fig. 4. MOI image of the magnetic flux penetration into a 3x3 mm^2 MgB_2 film, 600 nm thick, grown *in-situ* by PLD. The applied magnetic field of 50 mT was perpendicular to the (a, b) plane. The bright square contour is the edge of the film.

For the interpretation of the MOI we made use of numerical simulation of a perpendicular magnetic field B penetration into a rectangular film, characterised by B = μ_0H, and a highly non-linear I-V dependence, characteristic for HTS materials, at temperatures below T_c. This was based on one-dimensional integral equations for the sheet current, extended to describe time- and space-dependence [19,20,21]. The simulation was carried out in MATLAB environment, using Equation 1 [22,23]:

$$H_z(x,y) = H_a + \frac{J_c d}{4\pi}[f(x,y) + f(-x,y) + f(x,-y) + f(-x,-y)] \quad (1)$$

where:

$$f(x,y) = \sqrt{2}\ln\frac{\sqrt{2}P + a + b - x - y}{\sqrt{2}Q - a + b - x - y} + \ln\left|\frac{(P + y - b)(y - b + a)(P + x - a)}{(y - b)(Q + y - b + a)(x - a)(Q + x)}\right|$$

$$P = \sqrt{(a-x)^2 + (b-y)^2}$$

$$Q = \sqrt{x^2 + (b-a-y)^2}$$

And *d*, is the thickness, and *a* and *b* are the dimensions of the film. H_a represents the internal field from Ginzburg notation.

The simulation results are presented in Fig. 5. The sharp maxima of penetrated intensity of magnetic field H(x,y,t) at the edge of the film, and the sharp minima of H(x,y,t) at the current discontinuity lines represent the points where the self field of the supercurrents circulating in the film is zero, and therefore H(x,y,t) remains constant during the flux penetration, and equal to H_a. In the MOI image, these features are evidently similar with the simulation result, and this suggests that the film is homogenous.

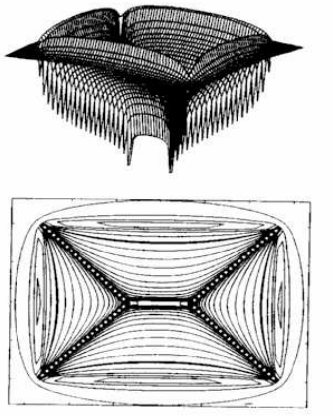

Fig. 5. Simulation of magnetic flux penetration into a thin film, applied perpendicular to (a,b) plane, using Equation 1.

The critical current density J_c versus magnetic field (B), parallel with the c-axis, was calculated from the measurements of magnetic moment versus applied field (B) for the films grown in-situ and ex-situ, using an extended Bean model, and the results are presented in Fig. 6. On the figure is also represented for comparison purposes the corresponding data for bulk MgB_2, obtained at 5 K. The values of J_c are presented here for comparative purposes. A reliable absolute value for magnetic J_c is difficult to obtain for thin films due to the highly inhomogenous field distribution, as shown above by numerical simulation.

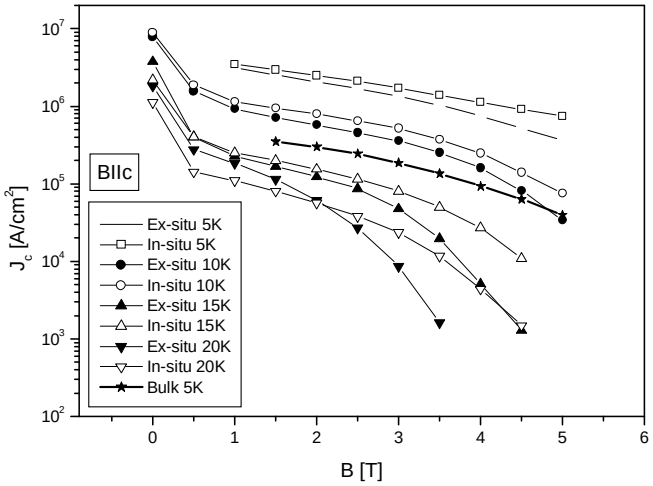

Fig. 6. Magnetic critical current density at different temperatures for MgB_2 film grown in-situ by PLD, and for MgB_2 film grown ex-situ, as described in text, as a function of applied magnetic field B, parallel to c-axis of the films.

Upon inspection of Fig. 6, we can see that the J_c of the *in-situ* grown films is higher at all measured temperatures than the *ex-situ* grown film, in spite of the higher transition temperature of the latter. This may be explained by the presence of a higher number of defects in the *in-situ* film as compared to the *ex-situ* film. Also, the field dependence of the *in*-situ film is better than for the *in-situ* film.

The J_c data at low temperature and low applied field is missing due to the strong magnetic flux instability (flux jump) under these conditions.

4. Conclusions

It was shown that the optimised PLD deposition conditions for MgB_2 thin films led to in-situ deposited films with strong pinning. Below 10K and large DC magnetic fields, applied parallel to the c-axis of the film, the irreversibility line of in-situ MgB_2 thin films is higher that of the bulk material. The critical current density J_c of in-situ thin films is less dependent on the applied magnetic field B than the current density J_c of an ex-situ MgB_2 film or bulk. In addition, it was shown by MOI that the in-situ films have homogenous pinning properties, a highly desirable feature for device applications.

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