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Pulsed-laser deposition of MgB_2 and B thin films

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ABSTRACT Thin films of the novel superconductor MgB_2 were deposited from an Mg-enriched MgB_2 target or by alternating ablation from Mg and B targets, depositing multilayers. The superconducting films were achieved in situ by a two-step process: deposition at low temperatures ranging from room temperature to 200 °C and subsequently heating to 600 °C. The color of the plasma originating from Mg or Mg-enriched MgB_2 targets during the deposition is an indicator of the constituents of the plasma and can be used to adjust the plasma parameters like pressure and energy density. The films showed a reduced critical temperature (T_c) compared to the bulk value (39 K), which is attributed to the small grain sizes and the relatively high base pressure of the system ($\sim 10^{-7}$ mbar) causing impurities (oxygen, carbon...). To investigate B oxidation and to determine the suitable deposition conditions for B, films made by pulsed-laser deposition (PLD) from B target were analyzed by XPS. The films are very sensitive to the ambient gas purity and the base pressure. We anticipate an improvement of T_c and the crystallinity of MgB_2 thin films by using PLD in high vacuum and with a high purity Ar and H_2 gas mixture.

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1 Introduction

The discovery of superconductivity in magnesium diboride (MgB_2) with critical temperature (T_c) of 39 K, announced in January 2001 [1, 2] has triggered an intensive worldwide research on this compound, first synthesized in 1950's [3]. Devices based on this material can operate at higher temperature than low-temperature superconductors using smaller and more convenient 30 K cryocoolers. This metallic like material is simpler and more stable over time compared to high-temperature superconductors, making it more attractive for applications. For example, in the case of superconducting quantum interference devices based on MgB_2 less noise is expected, giving a certain advantage for electronic circuits made in MgB_2 technology. The availability of superconducting thin films based on this material is therefore of great importance for many electronic applications as well as basic studies.

Although MgB_2 is a very simple compound, thin film fabrication of this material is not an easy task. The two main complicating factors in achieving the superconducting MgB_2 phase in the films are: the high vapor pressure of the magnesium, requiring the compensation for its loss, and the high sensitivity of magnesium and boron to oxidation, requiring very low oxygen partial pressures in the deposition system as well as very high purity of the ambient gas used [4]. Magnesium has extremely high vapor pressures at relatively low temperatures, for example 10^{-7} Torr at 210 °C, increasing to 1 Torr at 600 °C. As the melting point of Mg is 649 °C, generally Mg vapor sublimes from the solid, rather than evaporating from the melt [5], which makes this material very volatile.

2 Ablation of Mg and Mg-enriched MgB_2 target

As mentioned before, the color of the plasma can be used as an indicator for the species inside the plasma and it was found to be important for achieving the superconducting phase in the films.

The plasma-plume was changing the color depending on the ambient gas and its pressure and laser energy density (Table 1). By varying the background-pressure of argon gas, the color of the plasma-plume could be altered from intense green for low pressures, to bright blue for intermediate pressures and a mixture of green and blue for higher Ar pressures [6]. In the case of ablation of Mg-enriched MgB_2 targets, similar effects have been observed since the spectra consist mainly of neutral B and Mg lines (B I and Mg I-green line at 518 nm), with some contributions from their excited ions (B II and Mg II-blue line at 448 nm). The plasma emission in the visible range can be mainly attributed to Mg I and Mg II lines, because the most intense B lines belong to the UV spectral range [7]. As described in [7–9] the blue plasma is attributed to the presence of an ionic Mg II line, whereas the green color is attributed to the presence of a neutral Mg I line in spectra. The use of additional H_2 into Ar ambient gas has broadened the range of pressures where the Mg plasma was blue (Table 1). This broadening can be attributed to the getter effect

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Gas	p (mbar)	$E_{density}$ (J/cm^2)	Plasma color	
Ar (4.5)	0.10	6	Green	
	0.20		Blue	
	0.30		Green, blue*	
Ar + 4% H_2 (6.0)	0.05	6	Green	
	0.10		Blue, green**	
	0.15		Blue, green**	
	0.20		Blue	
	0.25		Blue	
	0.30		Blue	
	0.35		Blue, green**	
	0.40		Blue, green**	
Ar + 4% H_2 (6.0)	0.10	13	Bright blue	
Ar (4.5)			Blue, green**	
Ar + 4% H_2 (6.0)	0.10	13	Bright blue	
		10	Blue, green**	↓ Increasing
		8	Blue, green**	green
		6	Blue, green**	contribution
		4	Blue, green**	

* Denotes a mixture of dominating green plasma and some blue parts

** Denotes a blue plasma color with a presence of green color in outer shell as well as sometimes in its core

TABLE 1 Dependence of the color of Mg plasma on ambient gas, gas pressure, and laser energy; 4.5 and 6.0 correspond to gas purities of 99.995% and 99.9999%, respectively

of hydrogen towards residual oxygen lowering the oxygen partial pressure in the chamber. A similar effect has been observed for Ar + 4% H_2, both purities 99.995% and 99.9999%. The blue plasma with green parts at 13 J/cm^2 laser energy density in Ar environment turned into a bright blue at the same energy density in Ar + 4% H_2 (purity 99.9999%, Table 1), which clearly illustrates that the additional hydrogen-gas significantly increases the blue component in the plasma. Decrease of the laser energy density at the target caused the increase of the green halo in the plasma, leading to the conclusion that the sufficient energy density is needed to produce a blue plasma.

The optimal Ar or mixture of Ar and H_2 pressures to obtain the desired blue plasma depends on the system used (i.e. due to the difference in the laser parameters), which explains the different pressure values achieved in systems used by different researchers. From our experiments we concluded that a certain threshold of both laser energy density and deposition pressure is needed to achieve a higher degree of the ionization of plasma. A higher ambient pressure leads to an increase in recombination of Mg ions and therefore an increase of the neutral Mg I line present in the plasma. However, more spectroscopic measurements should be done on Mg plasma to confirm these anticipations.

It can be concluded that the color of the Mg plasma is very sensitive to deposition parameters, i.e., laser energy density, ambient gas and its pressure, and should be adjusted to allow for sufficient ionic emission. The pressure of the ambient gas (Ar or Ar + 4% H_2) also strongly influences the plasma dynamics in plasmas originating from Mg or Mg-enriched MgB_2 target. According to experimental observations, the gas pressure for a given laser energy should be tuned to achieve the blue color that is favorable for formation of the superconducting phase in MgB_2 thin film deposition.

Substrate	$p_{background}$ (mbar)	Gas	p_{dep} (mbar)	Results
Al_2O_3	3×10^{-7}	Ar	0.22	B_2O_3
(c-plane)	4×10^{-8}			
Si	1×10^{-7}	Ar	0.22	B_2O_3
(1%) HF	3×10^{-8}	Ar + 4% H_2(4.5)	0.2	B:O = 0.77 : 0.23
(etched)	5×10^{-9}	Ar + 4% H_2(4.5)		B:O = 0.82 : 0.18
	5×10^{-9}	Ar + 4% H_2(6.0)		B:O = 0.89 : 0.11

TABLE 2 Boron to oxygen ratio (from XPS data) in the films prepared by PLD of boron target in different background pressures and ambient gases at room temperature; 4.5 and 6.0 correspond to gas purities of 99.995% and 99.9999%, respectively. The presented results are determined from the depth XPS profile, i.e., inner part of the film when the amount of B and other elements saturate to avoid the surface effect

3 PLD of Boron

To investigate the sensitivity of boron to oxidation, pulsed-laser deposition of boron was done (Table 2). A boron target (purity 99.9%) was ablated for 10 min at 25 Hz in 0.22 mbar of Ar (purity 99.995%) or in 0.2 mbar of Ar + 4% H_2 (purity 99.995% and 99.9999%). The films were deposited on Al_2O_3 (c-plane) or on Si (where the surface SiO_2 was removed by etching with 1% HF) in base pressures ranging from 10^{-7} to 10^{-9} mbar [10]. The deposition rate of boron was about 10 nm/min.

The ablation in Ar resulted in the formation of B_2O_3 films, as revealed by XPS measurements on the films on Si and by the optical transparency of the films on Al_2O_3. The presence of B_2O_3 on Si leads to the conclusion that the oxygen from the substrate does not play a crucial role and that the oxygen is mainly coming from the background atmosphere in the chamber, possibly in the form of residual water vapor. The XPS measurements of films prepared using a base pressure of 10^{-8} mbar and Ar + x4 H_2 (purity 99.995%) resulted in intensity ratio of boron 1s line to oxygen 1s line of 0.77 : 0.23 (Table 2 and Fig. 1). The B : O ratio has been increased to

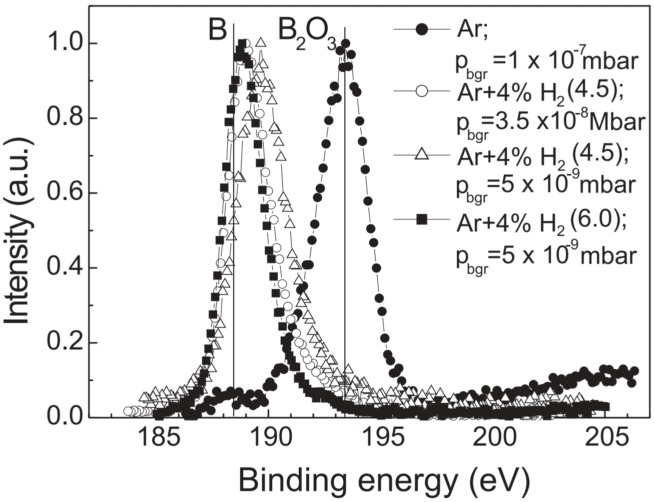

FIGURE 1 XPS measurement of samples deposited on Si (1% HF etched substrate) in different background pressures and ambient gases (shown in Table 2). The intensities of B 1s peak are normalized. p_{bgr} denotes the background pressure. *Solid lines* present the literature values for B (188.3 eV) and B_2O_3 (193.3 eV) peaks from NIST XPS database [12]

0.82 : 0.18 using a base pressure of 5×10^{-9} mbar in the system. It can be concluded that the addition of hydrogen-gas to Ar significantly reduces the amount of residual oxygen and consequently the amount of B_2O_3 present in the film, allowing the formation of B. The higher vacuum conditions increase the amount of B as well. A significant increase of the amount of B (almost 0.9 : 0.1 of B to O ratio), achieved in Ar + 4% H_2 (purity 99.9999%) and base pressure of 5×10^{-9} mbar, suggests that the use of higher purity Ar + 4% H_2 gas are fruitful in the growth of MgB_2 films in combination with ultra-high vacuum conditions prior to MgB_2 deposition.

We noticed a shift of the position of the B peak compared to values mentioned in literature. Maximum of the average of all O1*s* peaks originating from B_2O_3 (533.0 eV [11]) in the depth profile for each film was taken as a reference peak in the XPS analysis. An inaccuracy in its determination could cause the shift of the boron peak from literature value of B (188.3 eV [12]) in Fig. 1. There is also a possibility that oxygen does not entirely come from B_2O_3 compound, which is an additional reason for an inaccuracy, i.e., shift of B peak. The broadening of the peaks can be attributed to the possible reaction of B with carbon (up to 10%) and oxygen (making other oxides than B_2O_3) and formation of some compounds, which peaks overlap or superposition with the B peak. For example, binding energy of B_4C is 186.9 eV [12] and B_xO ($1 < x < 6$) is 188.0 eV [12]. The presence of these compounds could not be detected in XPS data due to their overlap and/or superposition with B peak.

Summarizing the results, the large affinity of boron and magnesium to oxygen emphasizes the need of a base pressure lower than 10^{-9} mbar and in combination with high purity Ar and H_2 gas mixture as an ambient gas could minimize the impurities in the films.

4 MgB_2 thin film deposition

Pulsed laser deposited MgB_2 films were prepared in two ways: by depositing from an Mg-enriched MgB_2 target (where the excess of Mg is used to compensate for loss of volatile Mg during deposition) and by growing multilayered films of Mg and B. The procedure is described in more details in [4, 13, 14] and in short will be presented here. The substrates used were Si, SiC, $SrTiO_3$, Al_2O_3 (*c*-plane and *r*-plane), and MgO. Most of the experiments were carried out on MgO substrates.

Prior to film deposition, preablation of Mg has been done to reduce the amount of residual oxygen in the chamber due to the Mg getter effect of oxygen. The superconducting films were achieved in situ by a two-step process: deposition at low temperatures ranging from room temperature to 200 °C and subsequently heating to 600 °C to form the correct phase. To avoid Mg-loss, the total annealing procedure was maintained short and in temperature range between 350 °C and 600 °C, keeping the sample in a pulsed (5 Hz) Mg plasma [14]. During deposition care was taken to ensure the blue Mg plasma, allowing the formation of the superconducting phase (as discussed above). PLD from Mg-enriched MgB_2 was typically carried out for 6 min at 10 Hz at an energy density of 4 J/cm^2, in an Ar-background pressure of 0.17 mbar, resulting in a thickness of about 200 nm. On the other hand, multilayers were formed by alternating ablation of a Mg target for 1 min at 10 Hz and boron metal for 3 min at 25 Hz, in an Ar pressure of 0.22 mbar.

The films grown at 200 °C showed T_c's of 26–27 K, which were a few degrees higher comparing to the T_c of the films prepared at room temperature. Films made at 300 °C were not superconducting at all [14]. X-ray diffractometry reveals no or hardly any MgB_2 peaks for our films, indicating that the films are polycrystalline with very small grain sizes (smaller than 5 nm). This reduced T_c compared to the bulk value is at least partially attributed to the very small grain sizes of MgB_2, the presence of MgO inclusions and to possible impurities in the starting material.

The multilayered films had a slightly higher critical temperature ($T_{c,0} \sim 28$ K), possibly due to the use of metallic targets as pure precursors as compared to sintered Mg-MgB_2 targets. According to the XPS results of PLD of boron described above it can be assumed that B_2O_3 films were formed between the Mg layers, which possibly melted partially during annealing at 600 °C (the melting point of B_2O_3 is 450 °C), reacted with Mg and formed the MgB_2 phase with MgO inclusions, resulting in superconducting films with a reduced critical temperature. Here, also no MgB_2 peaks were observed in X-ray diffraction pattern.

The experiments were preformed in the system with a relatively high base pressure of 10^{-7} mbar, which can cause the presence of the impurities in the films. According to the XPS analysis of the boron films, which showed the need of high vacuum, some improvement in the film quality could be expected by deposition in a chamber with a high vacuum and high purity gas mixture of Ar and H_2. A more promising approach towards the increase of T_c would be the formation of multilayers, since the purer targets are used as the precursors. Our attempts in this approach drew our attention to the time used for changing the targets in the deposition of multilayers, which plays a very important role. It should be as short as possible (in our case about a few seconds) to reduce the exposure time of a new layer to residual oxygen since both, Mg and B, are very easy to oxidize. The oxidation of boron by deposition at room temperature could be partially solved by annealing above the melting point of B_2O_3, which has been already achieved in multilayer deposition. However, the oxidation of Mg is much more harmful for the sample, due to the very high melting point of MgO (2852 °C). In our last experiments in ultra-high vacuum and high purity gas mixture of Ar and H_2 the time between ablation of Mg and B target was about 12 times longer compared to the one made in the chamber with 10^{-7} mbar base pressure (due to the different configuration of the system), causing the formation of transparent layers on Al_2O_3 substrates, as a signature of oxidized Mg and B layers. Reducing the time used for changing the targets could lead to the reduction of the oxidation of the Mg and B layers.

5 Conclusions

MgB_2 films are formed by a two-step method: deposition at low temperature followed by annealing at 600 °C. They have a reduced T_c compared to the bulk value, possibly due to the presence of the impurities in the film as well as in the starting materials and also due to the very small grain sizes of MgB_2. In the deposition of MgB_2 thin films, the high volatility of Mg as well as very high reactivity of Mg and B with the residual oxygen are complicating factors. To compensate for Mg loss due to its volatility, extra Mg in the PLD target was used. However, to avoid the reaction of Mg and B with oxygen, deposition should be performed in an ultra-high vacuum and a high purity Ar and H_2 mixture. In the case of multilayer formation, the time between changing the targets should be as short as possible to prevent additional oxidation of the newly deposited layers.

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