MgB_2 Thin Films and Josephson Devices

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***Abstract*—Since the recent discovery of superconductivity in MgB_2, various groups worldwide have been actively studying the growth of thin films based on this material. Impressive progress has been made, but various materials science challenges are still left to be solved. Guided by our own activities in this field, and reports presented in the literature, we reflect here on those challenges and possible ways for further improvement.**

Being important ingredients for many electronic applications, fabrication of Josephson devices and nano-structures in MgB_2 thin films will furthermore be described.

***Index Terms*—Josephson junction, MgB_2 thin films, pulsed-laser deposition, SQUID.**

I. Introduction

THE two most important challenges faced in growing *in situ* high-quality MgB_2 thin films are arguably the high magnesium and boron reactivity with oxygen, and the Mg volatility. To overcome these difficulties special measures to the thin film fabrication process are required. Many groups have introduced various ingenious concepts, which have enabled a steady progress in the quality of the obtained films. This process is still far from being finished. After the enhancement of the critical temperature T_c to levels approaching the bulk T_c of 39 K, the next challenge will be to enhance the crystallinity and decrease the defect density, preferably by establishing methods for growing epitaxial films.

Based on our own experiments we reflect here on the various challenges faced and possible ways for further improvement, as well as our research on Josephson devices based on this material.

II. Thin Film Preparation

Ideally one would like to grow MgB_2 thin films at a high temperature, forming the right phase in a single step without an additional annealing. Due to the volatility of Mg (vapor pressure is 1 mm Hg at 620°C) this ideal situation can only be reached with an extreme Mg/B flux-ratio during growth [1], [2]. Hence, a two-step process is adopted in which a precursor film undergoes an additional high temperature annealing step. The annealing can be done *ex-situ* [3], [4], but in order to obtain well-controlled growth and smooth films *in-situ* methods have been developed by us [5]–[7] and various other groups [4], [8].

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TABLE I
Pulsed-Laser Ablation of Boron Target at Room Temperature in Different Background Pressures andGas Environment

Substrate	$P_{background}$ (mbar)	Gas	p_{dep} (mbar)	Results
Al_2O_3 (c-plane)	3×10^{-7}	Ar	0.22	B_2O_3
	4×10^{-8}			
Si (1 % HF etched)	4×10^{-8}	Ar	0.22	
	3×10^{-8}	Ar + 4 % H_2	0.2	85 % B 15 % B_2O_3

Our pulsed laser deposited MgB_2 films were prepared [5]–[7] 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 substrates used were Si, SiC, $SrTiO_3$, Al_2O_3 (c-plane and r-plane), and MgO.

The studies of the influence of the deposition temperature were done on the films made on MgO substrates. The films were deposited at room temperature, 200°C and 300°C using an Mg-enriched MgB_2 target. The pulsed laser deposition was typically carried out for 6 min at 10 Hz at energy density of 4 J/cm^2, in an Ar-background pressure of 0.17 mbar, resulting in a thickness of about 200 nm. The high temperature-annealing step was performed by heating the films to $T_{\rm ann} = 600$°C, keeping the temperature fixed at this value for a few minutes and cooling down to room temperature, all in 0.22 mbar of Ar. To avoid Mg-loss, the total annealing procedure was maintained short and in the temperature range between 350°C and 600°C the sample was kept in a pulsed (5 Hz) Mg plasma [6], [7]. The films grown at 200°C showed T_c's of 26–27 K, which was a few degrees higher comparing to T_c of the films prepared at room temperature. On the other hand, films made at 300°C were not superconducting at all [7].

The multilayered films, grown from metallic Mg and B targets on MgO substrates at room temperature and annealed at 600°C [6], [7], 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.

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.

Besides the Mg-volatility, a further major challenge in growing MgB_2 thin films is the high magnesium and boron reactivity with oxygen.

To investigate the role of oxidation, pulsed-laser deposition of boron was investigated in more detail (Table I). A boron target was ablated for 10 min at 25 Hz in 0.22 mbar of Ar or in 0.2 mbar of Ar + 4% H_2. The deposition was done on Al_2O_3 (c-plane)

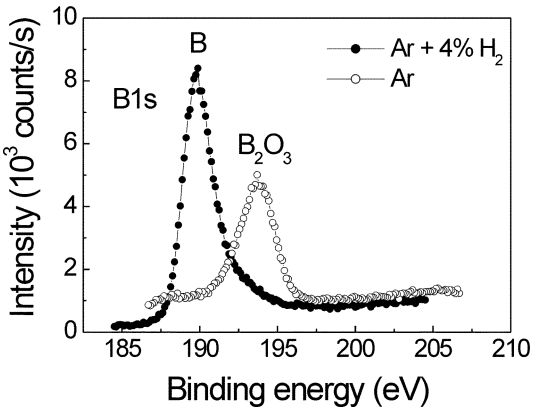

Fig. 1. XPS measurement of the samples deposited on Si (1% HF etched substrate) shown in Table I. The sample surface was cleaned by Ar ion milling. The closed circles present the sample made in Ar $+ 4\%$ H_2 and the open ones in an Ar environment.

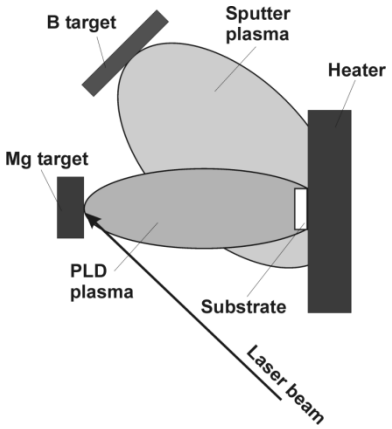

Fig. 2. Schematic view of the combined PLD and sputtering technique.

or on Si (where the surface SiO_2 was removed by etching with 1% HF) in base pressures of 3×10^{-8} mbar [9]. 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 entirely coming from the background atmosphere, possibly in the form of residual water vapor. The large affinity of boron and magnesium to oxygen emphasizes the need of a high vacuum base pressure in the order of 10^{-9} mbar in the chamber. This is also in line with the experiments of Ueda *et al.* [10], who obtained up to now the highest T_c of 36 K for in situ grown MgB_2 thin films by MBE and e-beam evaporation in systems with a base pressure of 10^{-9} to 10^{-10} mbar.

Interestingly, films made in Ar$+4\%$ H_2 contained 85% of unbound B (Fig. 1), suggesting that the addition of hydrogen-gas can be fruitful in the growth of MgB_2 films.

In the case of multilayers formed by the alternating ablation from Mg and B targets, superconducting thin films were achieved, although according to the XPS results described above, it can be assumed that B_2O_3 films were formed between the Mg layers. Since the samples were annealed at 600°C to form the superconducting phase, it is conceivable that B_2O_3 melted partially during annealing (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. These experiments were done in Ar environment and it can be expected that the deposition in mixture of Ar and H_2 can result in an increase of T_c.

The maximum observed T_c we obtained for MgB_2 thin films prepared *in-situ* by pulsed-laser deposition, is 28 K. 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.

As mentioned above, we have used Mg-enriched MgB_2 targets to compensate for the Mg-volatility. In an alternative approach we propose here a new concept for MgB_2 deposition (Fig. 2), which combines two techniques: sputtering of boron and pulsed-laser deposition of magnesium. Using this approach the Mg/B flux ratio can be adjusted. The low heat conductivity of boron easily causes splashing during PLD of boron, therefore, sputtering seems to be a better way of depositing this material. In experiments done by Ueda *et al.* [9] the high volatility of Mg limits the deposition temperature to about 320°C and requires an extremely high Mg flux. In this new concept, we are able to vary the Mg flux independently from the B flux by adjusting the laser frequency and the shape of the plasma. The high Mg flux is expected to allow higher deposition temperature, which is foreseen to lead to a better crystallinity of the films. The proposed approach is best combined with the earlier mentioned high vacuum and gas mixture of Ar and H_2.

III. Josephson Devices

Soon after the discovery of superconductivity in MgB_2, spectroscopic studies were performed on this material and a dc Josephson current was observed in point-contact junctions [11]. Apart from these fundamental studies, MgB_2 is interesting for application in Josephson electronics and SQUIDs and first realizations have already been reported [12]–[14].

Besides the larger critical temperature of MgB_2 as compared to the low-T_c material, a further positive aspect is the larger charge carrier density of MgB_2 than the high-T_c materials, which is deemed to be beneficial, *e.g.*, for the noise properties of Josephson devices. Furthermore, taking a multiband nature of superconductivity and the two different gaps of MgB_2 into account, large I_cR_n products are feasible, which was recently pointed out by Brinkman *et al.* [15]. For tunneling in the direction of the a–b plane of MgB_2 an I_cR_n product of 5.9 mV is predicted and 4.0 mV for tunneling in the c axis direction.

A. All-MgB_2 Multilayer Junction

As a first step toward MgB_2 Josephson electronic circuitry we have realized all-MgB_2 multilayer junctions in a ramp type configuration. The electrodes were made of MgB_2 films deposited from an Mg-enriched MgB_2 target and a 12 nm MgO layer formed the junction barrier layer. The details of the fabri-

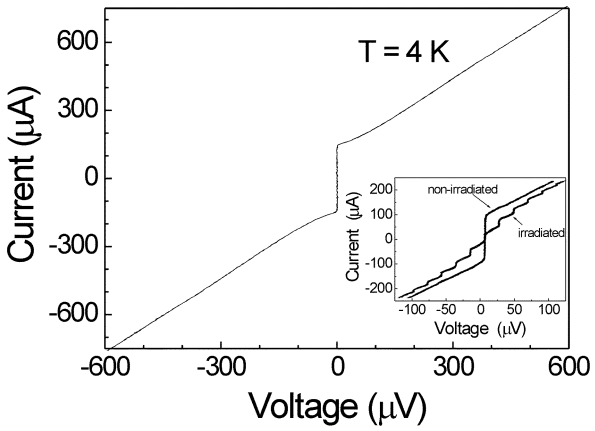

Fig. 3. Current–voltage characteristics of a 7 μm wide junction measured at 4 K. The inset shows Shapiro steps that appear by microwave irradiating the junction at 10.0 GHz (from [11]).

cation and the characterization of the junction are described in [13].

The nonhysteretic current–voltage $(I$–$V)$ characteristic of a 7 μm wide junction at $T = 4$ K is depicted in Fig. 3 and follows the behavior that is expected from the Resistively Shunted Junction (RSJ)-model. The resulting I_cR_n product of 130 μV at 4.2 K is lower than the theoretical expectations [15].

The critical current was found to modulate by applying a magnetic field perpendicular to the current direction and parallel to the substrate. A suppression of the critical current by up to 70% was observed. The $I_c(H)$-dependence differs from the Fraunhofer dependence that is expected for a small junction with a uniform current distribution, indicating the nonhomogeneity of the barrier. The ac Josephson effect is shown in the inset of Fig. 3, where a complete modulation of the supercurrent and the formation of Shapiro steps at multiples of $V = 20.7$ μV were observed by microwave irradiating the junction at 10.0 GHz at $T = 4.2$ K.

For ramp-type contacts that were prepared without a MgO barrier layer, a very high critical current density of 3×10^6 A/cm^2 at $T = 4.2$ K was observed, implying that the interface region has good superconducting properties even after Ar ion beam milling, and that they will not affect the transport characteristics of Josephson junctions as is the case for high-T_c contacts.

The outcome of this study underlines the need for a smooth and epitaxial MgB_2 film as base electrode and motivates further investigations into the *in-situ* film growth procedure.

B. MgB_2 SQUIDs Based on Nanobridges

We have realized MgB_2 SQUIDs based on nanobridges that act as weak links in a superconducting SQUID loop. The nanobridges are patterned by Focused Ion Beam etching in 200 nm MgB_2 thin films. The typical width of the nano bridges is 70 nm, and the length is 150 nm. The details of the fabrication and characterization are described in [14].

The transition temperature of the structure was 22 K, which is comparable to the T_C value of the unpatterned film. The voltage modulation as a function of the applied magnetic field is observed [14]. The large critical current densities of 7×10^6 A/cm^2 of these bridges confirm that the grain boundaries in our polycrystalline films show strong link behavior [16], and that high-quality nanostructures can be realized in MgB_2.

IV. Conclusion

The *in-situ* preparation of superconducting MgB_2 thin films by pulsed-laser deposition is discussed in this paper. The reduced transition temperature of 28 K as compared to the bulk value (39 K) is possibly due to the small MgB_2 grain-size, impurities present in the starting material and MgO inclusions formed in the films. Combined PLD from an Mg target and sputtering from a B target is proposed as a possible technique for the formation of epitaxial MgB_2 thin films.

Films prepared in a two-step process from an Mg-enriched MgB_2 target were used to fabricate multilayer Josephson devices. All-MgB_2 ramp-type Josephson junctions with a 12 nm MgO barrier-layer were realized, showing RSJ-like current–voltage characteristics. The dc-Josephson effect was demonstrated by the observation of the critical current and its modulation by applied magnetic fields. The ac-Josephson effect has been demonstrated by the appearance of Shapiro steps under applied microwave irradiation.

MgB_2 ring-structures incorporating nanobridges display Josephson quantum interference effects, which forms the basis for the creation of an all MgB_2 SQUID. These nanostructures have outstanding critical current densities of 7×10^6 A/cm^2 at 4.2 K.

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