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Growth and properties of high quality MgB_2 Superconducting Thin Films

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Abstract
The discovery of superconductivity in the metallic compound MgB_2 with its transition temperature at 39K has stimulated considerable interest in the area of superconductivity. The recent discovery of superconductivity near 40 K in MgB_2 has generated much interest in the properties of this simple inter-metallic compound. To realize superconducting Josephson devices based on this material that can be implemented further in electronic circuits, crystalline grown MgB_2 thin films are preferred. Thermodynamics calculations indicate that Al_2O_3 is chemically stable under the in situ deposition condition for MgB_2. In this paper, we study the optimum conditions for superconductor MgB_2 thin film growth on various substrates.

Keywords: MgB_2, superconductivity, thin films

1. Introduction
Smooth, single-phase, crystalline grown superconducting MgB_2 thin films are desired for Josephson device fabrication and their implementation in electronic circuits. To achieve a stable MgB_2 phase and crystalline films a deposition at high substrate temperatures (e.g. 600-800 °C) is necessary. This brings up a number of difficulties that need to be surpassed. The high Mg vapor pressure makes this element very volatile and a very high Mg pressure is needed to overcome the Mg loss. Furthermore, the very low Mg sticking probability at temperatures higher than 300° C requires even higher Mg overpressure. Additionally, Mg and B show very pronounced affinity to the residual oxygen in the deposition chamber, making the realization of MgB_2 films more complicated. A certain Mg vapor pressure is necessary to make MgB_2 thermodynamically stable at high temperatures. The volatility of Mg, however, also brings a benefit. It allows the automatic composition control in the so- called adsorption- controlled growth [2]. As long as the Mg to B ratio is large enough, the composition in the film will remain1: 2 and extra Mg will be in the gas phase and pumped away.

This exciting discovery immediately attracted the attention of many research groups worldwide and since then hundreds of research papers have been published on MgB_2 and MgB_2-based devices. Kim et al. [1] investigated the sticking coefficient of Mg during MgB_2 thin film fabrication. The Mg sticking coefficient drops to almost zero above 300 °C. On the other hand, boron shows no change in the sticking coefficient as temperatures changes. The low sticking probabilities imply that there is only a small probability that Mg reacts with B to form the non-volatile MgB_2 compound. Therefore, a very high Mg flux is needed to ensure enough Mg to react with B.

The reactivity of Mg to oxygen is illustrated in [4]. They showed the Gibbs energy of Mg reacting with oxygen to form MgO. Compared to silicon, which oxidizes very easily, the value of the Gibbs energy is even more negative indicating that Mg reacts very strongly with oxygen. In the case of vacuum- deposition

techniques, an ultra- high vacuum system is needed to make the deposition successful, because the oxygen contamination in non- UHV systems can severely influence the deposition of MgB_2 films [3].

Ueda et al. [5] reported the role of the residual gases in the growth of MgB_2 by Molecular Beam Epitaxy (MBE). Their experiments showed that the residual oxygen is very harmful to the film growth even with a partial pressure as low as $1x10^{-9}$ mbar. Residual hydrogen and nitrogen, on the other hand, have a negligible or even a slightly favorable effect on the MgB_2 film growth.

An improved hybrid physical chemical vapor deposition (HPCVD) method for the preparation of magnesium diboride (MgB_2) films is proposed. The deposition of MgB_2 films on a polycrystalline Al_2O_3 substrates is obtained by the reaction between evaporated magnesium atoms and boron atoms that decompose from diborane near the heaters. The superconducting MgB_2 films show a transition temperature at 38.5 K and a zero-resistance temperature at 38 K. The critical current density of the films is 10^5 A/cm^2[13]. By using hybrid physical-chemical vapor deposition (HPCVD) method, MgB_2 thin films were fabricated on silicon substrates with buffers of alumina grown by using atomic layer deposition method. The growth conditions were in a range of growth temperatures of 500–600 °C and under the reactor pressures of 25–50 Torr [12].

The growth of high-quality MgB_2 films by thermally decomposing decaborane ($B_{10}H_{14}$) in Mg vapor. We grew MgB_2 films on *c*-cut sapphire substrates held at 400–450 °C by supplying vaporized $B_{10}H_{14}$ into a pocket heater with high Mg vapor pressure. The resultant films as thin as 100 nm showed strong and sharp *c*-axis lattice peaks in X-ray diffraction, indicating nearly ideal epitaxial growth [14].

The growth of MgB_2 films by pyrolysis of decaborane ($B_{10}H_{14}$) in Mg vapor was discussed by yamazaki and Naito [15]. Increasing the growth temperature, this reaction becomes noticeable and leads to the formation of MgO and $Mg_{1-x}Al_xB_2$, which deteriorates the properties of resultant MgB_2 films. Recently, Superconducting MgB_2 thin films with different thicknesses were fabricated by excess Mg using sequential electron beam evaporation technique. The flux rate of Mg and B were chosen as 3 nm/sn and 0.5 nm/sn respectively. The thickness of Mg/B layer was determined as 3/1 which causes an excess Mg for MgB_2 formation [16].

In this Paper, we explores the aspects of MgB_2 thin film growth with various substrates. To grow MgB_2 we supply Mg and B during the deposition. We are also interested to investigate the aspects of the deposition: the plasma formed by pulsed-laser ablation of Mg and Mg- enriched MgB_2 targets, and the influence of impurities by investigating the oxidation of B.

2. Experiment

2.1 Properties of Mg and Mg-enriched MgB2 plasma

Element Mg has a vapor pressure that is many orders of magnitude higher than that of B, and thus a relatively high pressure of Mg is needed to ensure the phase stability of MgB2 at the deposition temperature. Mg also reacts strongly with oxygen which can therefore contaminate the films and adversely affect their superconducting properties. These properties pose difficulties for most physical vapor deposition growth techniques. Thus it is also difficult to control the growth rate and the relative Mg and B fluxes to routinely achieve the correct phase.

Experimentally, it was clear that the color of the plasma (formed by pulsed- laser ablation of Mg and Mg-enriched MgB_2 target) was dependent on deposition conditions and varied from intense blue to green [6]. It was noticed that 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 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 targets. According to experimental observations, the gas pressure for certain 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.

2.2 Boron Oxidation

To study the influence of impurities, both, coming from the ambient gas and the deposition system, we investigated oxygen incorporation in the boron films. To investigate the sensitivity of boron to oxidation, films deposited by pulsed- laser deposition and RF magnetron sputtering from pure boron targets were analyzed by XPS. First, the films were prepared by pulsed- laser deposition using a 99.9% pure boron target (Table 1) for 10 min at 25 Hz laser frequency in 0.22 mbar of Ar or in 0.2 mbar of Ar + 4% H_2 (purity 99.995% and 99.9999%). The target- substrate distance was 4.2 cm, resulting in a deposition rate of ~ 10nm/min. We chose a Si substrate with removed native oxide layer to avoid the reaction of oxygen with B. The native oxide layer on the Si wafer was removed by etching the substrate in 1% hydrofluoric acid (HF). We used systems with different background pressures to investigate the sensitivity of B to residual oxygen [7].

The ablation in Ar resulted in the formation of B_2O_3 films, as revealed by XPS measurements on the films, which leads to the conclusion that the oxygen is mainly originating from the background atmosphere in the chamber, possibly in the form of residual water vapor. XPS measurements of films prepared in a base pressure of 10^{-8} mbar prior to deposition and Ar + 4% H_2 (purity 99.995%) as ambient gas resulted in an intensity ratio of the boron 1s line to the oxygen 1s line of 0.77: 0.23(Table 1 and Fig. 1). 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 prior to deposition (base pressure of $5x10^{-9}$ mbar) resulted in an increase of the B:O ratio of 0.82: 0.18. A significant increase of the amount of B (almost 0.9: 0.1 of B to O ratio), was achieved in Ar + 4% H_2 (purity 99.9999%) using a background pressure of $5x10^{-9}$ mbar.

Substrate	**$P_{background}$ (mbar)**	**Gas**	**P_{dep} (mbar)**	**Ratio (B:O)**
Si	$1x10^{-7}$	Ar	0.22	0:1
(1%HF etched)	$3x10^{-8}$	Ar + 4% H_2 (4.5)		0.77:0.23
	$5x10^{-9}$	Ar + 4% H_2 (4.5)	0.2	0.82:0.18
	$5x10^{-9}$	Ar + 4% H_2 (6.0)		0.89:0.11

Table 1: 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 XPS depth profile, i.e., inner part of the film (about 4 nm under the film surface)[1] when the amount of B and other elements saturate to avoid the surface effect.

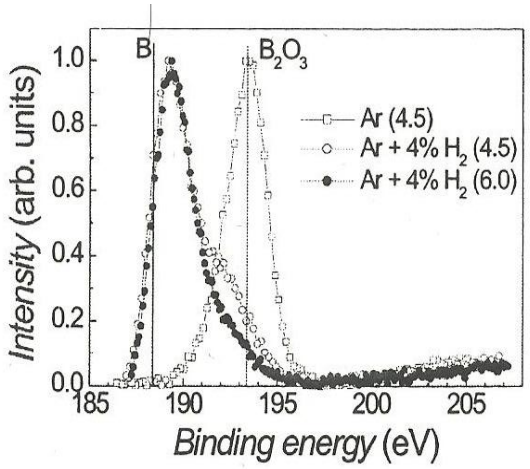

Fig. 1: XPS measurement of the samples deposited by PLD on Si in different background pressures and ambient gases (shown in Table 4.2). The intensities of the B1s peak are normalized. p_{bgr} notes the background pressure. Solid lines present the literature values for B (188.3 eV) and B_2O_3 (193.3 eV) peaks from NIST XPS Database.

3. Substrate Selection

The reproducibility and reliability of all Josephson devices will rely on the degree of epitaxy and smoothness of the MgB_2 thin films, underlining the need for an epitaxial growth procedure [8]. To achieve epitaxial growth, the films need to be grown at high substrate temperature (e. g. 600-800 °C). Therefore, it is necessary to choose a substrate, which does not react with MgB_2 film at the elevated temperatures.

The substrate choice is of utmost importance issue in epitaxial growth. MgB_2 has a hexagonal structure, with Mg and B planes stacked alternately along the c-axis, and therefore, it is understandable that the substrates with a hexagonal lattice at the surface provide better results [5]. Table 2 gives an overview of materials with hexagonal structure, which are suitable as substrates or interlayers to ensure the epitaxial growth of MgB_2. The a-to- a alignment between MgB_2 and Al_2O_3 results in ~ 23 % lattice misfit being unfavorable for the epitaxial growth. But, a 30° angular off the a-to- a alignment between the basal plane of MgB_2 and Al_2O_3 results in a smaller lattice misfit (~ 10%) between the MgB_2 thin film and the (0001) Al_2O_3 substrate that possibly allows the epitaxial growth [9]. Because of the smallest lattice misfit SiC is the most suitable material. Its elementary structural unit is a C- Si tetrahedron. SiC has over 170 polytypes, determined by the stacking sequence of the C- Si bilayer with a hexagonal structure [10]. If the first bilayer is called the "A'' position, the next bilayer can be placed in''B'' position. The stacking sequences for the polytypes 4H- SiC are AABB and for 6H- SiC are AAABBB [11]. Both have a hexagonal structure with lattice parameters close to the lattice parameter of MgB_2 (Table 2). An (0001) orientation(c-cut) of both polytypes provides a hexagonal lattice with a close lattice match to MgB_2.

The substrate cut defines the shape of the surface and its importance can be illustrated in the following example. Si (111), SiC, Al_2O_3(c- plane) and MgO (111) have a hexagonal surface, which makes them more

suitable for MgB_2 growth compared to, for instance, Al_2O_3(r- plane), $SrTiO_3$ (100) and MgO (100), which have square or rectangular surface crystallinity.

Besides lattice matching, the reactivity between substrate and thin film also has to be taken into account. It is concluded that MgO, SiC, AlN and TaN substrates are stable substrates for MgB_2 deposition with no reaction between Mg vapor and the substrate. Additionally, AlN and TaN have a rather small misfit with MgB_2 (Table 2). The Mg vapor partially reacts with the Si, ZrO_2 and TiN substrates. However, if the Mg pressure is low enough these substrates can remain stable in the Mg vapor. There are reactions between Mg vapor and SiO_2, Al_2O_3 and GaN substrates. It can be concluded that one of the most promising candidates of the substrates for epitaxial MgB_2 growth is SiC because of its perfect lattice match with MgB_2.

Material	Lattice parameters (Å)	Lattice misfit for a-to-a alignment
MgB_2	a = 3.086 c = 3.524	---------
Al_2O_3	a = 4.77 c = 13.04	-23%
TaN	a = 5.170 c = 2.890	-6.5%
GaN	a = 3.190 c = 5.189	-3.3%
AIN	a = 3.110 c = 4.980	0.80
Si	a = 3.800 c = 6.269	23%
TiB_2	a = 3.028 c = 3.228	1.8%
SiC (4H)	a = 3.073 c = 10.053	0.42%
SiC (6H)	a = 3.081 c = 15.12	0.16%

Table-2: List of some substrates and/or interlayer with a hexagonal structure, their lattice parameters and lattice misfit with a-axis lattice parameter of MgB_2. A positive sign of the lattice misfit denotes that the epitaxial film will be stretched in tension and a negative one means the film comprehension. The lattice parameters data originate from inorganic crystal structure database [12]

5. Conclusions

For achieving the epitaxial growth of MgB_2 thin films, needed for multilayered structures to be used in electronic devices, deposition at elevated temperatures is a prerequisite. A number of difficulties in thin film fabrication are faced then. The high Mg vapor pressure i. e. volatility of this element and low Mg sticking probability at elevated temperatures significantly limits the deposition temperature and subsequently influences the epitaxial growth. A high deposition temperature requires a very high Mg overpressure, i.e., high Mg flux, to compensate for its loss. This favors deposition techniques that can provide such a high Mg overpressure during deposition.

We showed that B is very sensitive to residual oxygen in the chamber and in ambient gas. A higher B flux is obtained in PLD from a B target compared to sputter deposition of B, which reduces the oxidation of B. To form MgB_2 with a very high B flux, even higher Mg fluxes are needed, which is not achievable by PLD. The color of the plasmas originating from Mg and Mg- enriched MgB_2 targets is an indicator of its constituents. The superconducting MgB_2 phase is reached by preparing the films in blue plasma, which is achieved by tuning the deposition parameters, such as the pressure of the ambient gas in the deposition chamber and laser energy density at the target. The optimum deposition parameters were about 0.2 mbar of the ambient gas at 6J/ cm^2. Thus the method should be easily extendable to completely *in situ* deposition of multilayer structures. This method can thus enable the development of films for many potential applications. Moreover, we anticipate extending this versatile and effective reactive deposition technique to the growth of other compounds of technological importance that are also very challenging to produce in thin film form by alternative growth techniques.

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