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Sputtered magnesium diboride thin films: Growth conditions and surface morphology

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ABSTRACT

Magnesium diboride (MgB_2) thin films were deposited on *C*-plane sapphire substrates by sputtering pure B and Mg targets at different substrate temperatures, and were followed by in situ annealing. A systematic study about the effects of the various growth and annealing parameters on the physical properties of MgB_2 thin films showed that the substrate temperature is the most critical factor that determines the superconducting transition temperature (T_c), while annealing plays a minor role. There was no superconducting transition in the thin films grown at room temperature without post-annealing. The highest T_c of the samples grown at room temperature after the optimized annealing was 22 K. As the temperature of the substrate (T_s) increased, T_c rose. However, the maximum T_s was limited due to the low magnesium sticking coefficient and thus the T_c value was limited as well. The highest T_c, 29 K, was obtained for the sample deposited at 180 °C, annealed at 620 °C, and was subsequently annealed a second time at 800 °C. Three-dimensional (3D) AFM images clearly demonstrated that the thin films with no transition, or very low T_c, did not have the well-developed MgB_2 grains while the films with higher T_c displayed the well-developed grains and smooth surface. Although the T_c of sputtered MgB_2 films in the current work is lower than that for the bulk and ex situ annealed thin films, this work presents an important step towards the fabrication of MgB_2 heterostructures using rather simple physical vapor deposition method such as sputtering.

1. Introduction

Among non-oxide superconductors magnesium diboride (MgB_2) has a record of high superconducting transition temperature ($T_c \sim 39$ K). The discovery of the novel superconductor MgB_2 raised great interest for its potential in both science and technology applications. MgB_2 is a good candidate for superconducting electronic application due to (1) the higher T_c compared to the conventional low-T_c superconductors, (2) large critical current density, and large coherence length (~5 nm) [1] compared to the high-T_c oxide superconductors. However, to realize these advantages in thin film form, several problems related to the materials have to be resolved. At present, the most important issue in the electronic application of MgB_2 is to develop the technology needed to produce and manipulate high-quality thin films. High-quality MgB_2 thin films, preferably deposited in situ, are necessary for hybrid heterostructures. It has been found that it is very difficult to maintain an environment for the in situ formation of the stoichiometric MgB_2 phase due to the extreme difference in the vapor pressures of Mg and B. Therefore, simple physical vapor deposition methods, such as sputtering and pulsed laser deposition, were not really successful in fabricating high-quality MgB_2 thin films.

Since the discovery of superconductivity in MgB_2, thin films have been fabricated in many different ways. In the early stages, the pulsed laser deposition method was mostly used to fabricate MgB_2 films [2–6]. Subsequently, e-beam evaporation [7], molecular beam epitaxy [8,9], sputtering [10–14], and chemical vapor deposition [15] methods have been explored. Since it is very difficult to maintain a stable environment for the in situ formation of the stoichiometric MgB_2 phase, most of the films were made by either ex situ diffusion of Mg in B precursor film [2,7,15] or in situ annealing [3–6,9,11,14]. The thin films made by ex situ annealing showed the T_c close to the bulk value (~39 K), but the thin films treated in situ showed lower T_c in general. According to the pressure–temperature phase diagram reported by Liu et al. [16], an extremely high deposition rate of Mg is necessary to get the stoichiometric MgB_2 phase in situ. The hybrid physical–chemical vapor deposition method has produced thin films with bulk T_c values [17]. Even higher T_c (>40 K) than the bulk value was reported in MgB_2 film in which it had a biaxial tensile strain [18].

Sputtering is a relatively simple method for the fabrication of thin film and has the potential for device application. The most ideal case for the application of MgB_2 thin films to electronic

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devices would be that the as-grown sputtered MgB_2 thin films deposited at low growth temperatures have a significant T_c value without a post-annealing process. However, as shown previously in other papers, this is still left as a very challenging problem.

To solve this problem, it is necessary to carefully investigate the role of each growth parameter and tune it to optimize the growth process. Although there were some previous works where the sputtering method was used, the systematic thorough study of the correlation between the growth conditions and physical properties, including transport, magnetic, and surface properties, was not done.

In this work, we fabricated MgB_2 thin films by a sputtering method and investigated the effect of various growth and annealing parameters on their physical properties. We also associated the superconducting properties of the MgB_2 thin films with surface morphology characterized by Atomic Force Microscopy (AFM). Our current work provides an important step towards the fabrication of MgB_2 thin films using a rather simple physical vapor deposition method, such as sputtering, by studying the correlation between the growth parameters and the physical properties. We propose a possible solution to the problem that the sputtering method contains for the optimized MgB_2 thin film growth.

2. Experimental

We used a conventional multi-target sputtering system to fabricate the MgB_2 thin films. The MgB_2 thin films were deposited on *C*-plane sapphire substrates using DC-magnetron sputtering of Mg at 50 W and rf-magnetron sputtering of B at 150 W. The base pressure of the deposition chamber was always lower than 2.0×10^{-7} Torr. Before the deposition, the substrates were chemically cleaned using acetone and methanol. Argon (Ar) pressure during the sputtering was 1.5 mTorr for the deposition at room temperature and 0.5 mTorr for the deposition at elevated temperatures. To improve the uniformity of the sample, the substrate was rotated during deposition. Due to a low sticking coefficient of Mg at high temperatures, MgB_2 films were deposited either at room temperature or at temperatures lower than 200 °C, and were followed by in situ post-annealing at a higher temperature. For most of the samples, a thick layer of Mg and a thin layer of B were deposited on top of the MgB_2 layer before annealing. A Mg capping layer was used to compensate for the Mg loss during the high temperature annealing and a B capping layer was used to prevent the Mg escaping from the films at high temperatures. For comparison, some of the samples were made without capping layers. After the deposition, the films were heated in situ at a rate of 3.44 °C/s to the annealing temperature. Annealing conditions were varied: temperature between 500 and 800 °C, Ar pressure between 2.0×10^{-2} and 0.1 Torr, and the annealing time between 5 and 60 min.

T_c was determined from a four-probe resistance measurement or an AC susceptibility measurement. Resistance of the sample was measured using either a Quick Dipper resistance probe or a Quantum Design Physical Property Measurement System (PPMS-9T). AC susceptibility was measured using PPMS-9T. The surface morphology of MgB_2 thin films was investigated using Multimode™ AFM. The images were taken for the various samples to explore the effects of substrate and annealing temperatures on the surface morphology. The RMS roughness and grain size were obtained and compared among the different samples.

3. Results and discussion

We report the results for two different sets of data. One set contains the thin films deposited at room temperature, while the other set contains the thin films deposited at elevated, but low growth temperatures (<200 °C).

3.1. Thin films deposited at room temperature

Thin films were deposited by the sputtering pure B and Mg targets at room temperature to be followed by in situ annealing. We grew our samples at room temperature to maximize the Mg sticking coefficient. In our sputtering condition, the Mg deposition rate was about 1 Å/s. As-grown samples at room temperature were metallic down to 1.9 K and did not show superconducting properties. Only after the as-grown films were annealed at higher temperatures were the superconducting transitions detected. We have investigated the effects of the sample structure and annealing conditions on the superconducting properties. The highest T_c was obtained for the films in situ annealed at 620 °C with Ar pressure of 100 mTorr giving a T_c of 22 K.

Several different types of structures were used to optimize the growth of MgB_2 precursor at room temperature. We fabricated (a) the single layer of co-deposited Mg and B, (b) the bilayer of Mg and B, and (c) the multilayer in which the layer of co-deposited MgB_x and the thin layer of Mg alternate. For the multilayer sample as shown in Fig. 1, Mg and B were co-deposited for 1.5 min to create the MgB_x layers and a very thin layer of Mg was deposited for 30 s between each layer of MgB_x so as to make up for any Mg loss during the annealing process. All three types of structures were covered with Mg/B capping layer for the in situ post-annealing. The thickness dependence of these capping layers will be discussed later.

The most effective structure was a multilayer of MgB_x and Mg. Referring to the Mg:B binary phase diagram [16], a Mg vapor pressure between 10^{-3} and 10 Torr is required to make the MgB_2 at a temperature of 620 °C. The Mg layers sandwiched between layers of MgB_x are assumed to provide this Mg vapor pressure at high temperatures. The T_c dropped from 22 to 15 K when we did not deposit the Mg sandwich layers (this structure is eventually the same as the single layer of co-deposited Mg and B). AFM data, discussed in a later section, supported the notion that the thin film deposited at room temperature was a mixture of Mg and B, and MgB_2 phase was developed during the post-annealing.

Since the MgB_2 phase was not formed at room temperature, we relied on a high temperature annealing process to form the phase. To optimize the annealing condition, we changed the parameters. The annealing conditions we have tested were (a) the temperatures between 500 and 800 °C, (b) Ar pressures between 10 mTorr and 0.1 Torr, and (c) the time varying from 5 to 60 min.

The T_c increased as the annealing temperature increased, but then started to drop above 630 °C. The sample became insulating when the annealing temperature became higher than 650 °C. At this temperature Mg would evaporate from the sample. It has been

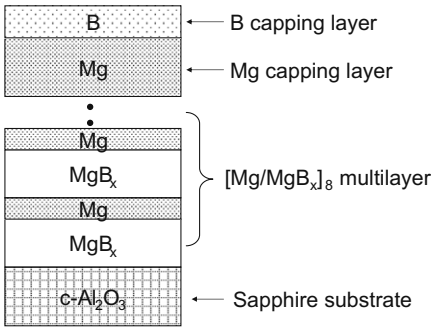

Fig. 1. Sample structure of the $[Mg/MgB_x]_8$ thin films deposited at room temperature.