Superconducting and Microstructural Properties of Two Types of MgB2 Films Prepared by Pulsed Laser Deposition

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Superconducting and Microstructural Properties of Two Types of MgB$_2$ Films Prepared by Pulsed Laser Deposition

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Abstract—Significant differences in superconducting and microstructural properties between two types of MgB$_2$ films prepared by pulsed laser deposition were determined. A very high H$_c2$ — T slope of 1.1 T/K was achieved in the in situ film. The J$_c$ — H curves of the in situ film also show a much weaker field dependence than that of the ex situ film. The magneto-optical (MO) images show that at 4 K the flux penetrates the in situ MgB$_2$ film through random paths, while for the ex situ film, the flux penetration pattern is mostly repeatable, indicating a defect-controlled flux penetration. Microstructural study (transmission electron microscopy and atomic force microscopy) revealed a relatively big grain size in the ex situ film. The correlation between the superconducting properties, microstructure and preparation conditions is discussed with regard to the two types of films.

Index Terms—Magneto-optic imaging, superconducting MgB$_2$ films, transmission electron microscopy.

I. INTRODUCTION

The two-gap phonon mediated superconductor MgB$_2$ has some very attractive properties and great interest has been focused on the preparation of MgB$_2$ thin films for both theoretical and application purposes. Shortly after the discovery of superconductivity in this material, MgB$_2$ thin films with bulk-like T$_c$ were achieved by ex situ annealing of a boron or Mg-B precursor film in Mg vapor [1], [2]. Kang and co-workers optimized the ex situ annealing conditions by fine-tuning the annealing temperature and time, and a very high J$_c$ of ~ 10$^7$ A/cm$^2$ at 5 K, 0 T with a weak field dependence was obtained [3]. Eom and coworkers found that a high oxygen level in the MgB$_2$ film prepared by a two-step ex situ annealing procedure significantly improved the J$_c$ in high fields [2]. Zeng et al. developed an in situ hybrid physical-chemical vapor deposition (HPCVD) method to grow high quality MgB$_2$ film epitaxially [4]. The J$_c$ value of their MgB$_2$ film reached 3.5 × 10$^7$ A/cm$^2$ at 4.2 K, 0 T, but it dropped rather quickly to 10$^5$ A/cm$^2$ as the field increased to 4 T. As-grown and in situ annealed films, prepared by pulsed laser deposition (PLD), molecular beam epitaxy (MBE) or magneto-sputtering employing much lower substrate temperatures and shorter annealing times, generally show a small-grain feature and poor crystallization [5]–[9]. This category of films has suppressed T$_c$, but the J$_c$ properties are quite good in high fields, which indicates strong pinning and intra- or inter-band scattering due to a high disorder level in the films. As can be seen, the properties of MgB$_2$ thin films vary significantly with different preparation processes, which are closely related to the variety of microstructures and impurity levels of those MgB$_2$ films. A study of this relationship could be relevant to the optimization of the film preparation.

In this paper, we report a comparative study on in situ and ex situ annealed MgB$_2$ films prepared by pulsed laser deposition. The relationship between the superconducting properties and the microstructure is investigated, and the influence of the preparation conditions on the two types of MgB$_2$ films is discussed.

II. EXPERIMENTAL

In the preparation of the in situ annealed film, the precursor film was deposited on a 250°C Al$_2$O$_3$ – R substrate from a stoichiometric MgB$_2$ target (84% density). A pulsed excimer laser beam (λ = 248 nm) with energy fluence of 300 mJ/pulse was focused to a 8 mm$^2$ ellipse spot on the target. During the deposition process, the atmosphere was 120 mTorr higher purity Argon. An 800 nm Mg cap layer was deposited on top of the precursor film to compensate the Mg loss due to annealing. The film was then heated to 685°C in 12 min and kept at this temperature for 1 min in a 1 atm Ar atmosphere. For the ex situ annealed MgB$_2$ film, a boron precursor film was deposited from a boron target (~40% density) onto an Al$_2$O$_3$ – R substrate in a 10$^{-7}$ – 10$^{-6}$ Torr vacuum. The precursor film was then annealed at 900°C for 30 min in a sealed stainless steel tube with Mg pellets. The details of the preparation are described in [10].

The transport measurements were carried out on a PPMS-9T magnetometer system (Quantum Design), using a standard 4-probe method and a dc current density of 1 A/cm$^2$. The zero-field-cooled (ZFC) magnetization vs. temperature curves and magnetization hysteresis loops of the films were measured on an MPMS-5 T magnetometer. In each measurement the applied field was perpendicular to the film plane. The J$_c$ was calculated from the magnetization loops using the Bean model. The upper critical fields (H$_c2$) in different temperatures were obtained using 90% $\rho_T$ points in the resistivity-temperature (ρ – T) curves measured in different fields.

The MO imaging was carried out at the University of Oslo, employing a bismuth substituted yttrium iron garnet indicator.
film [11]. The indicator film was placed directly on top of the MgB2 film. The magnetic field \(H_a\) was applied perpendicularly to the film surface. All images were taken at a constant temperature after samples have been zero-field cooled. Transmission electron microscopy (TEM) images were taken in a 200 KV JOEL2010 TEM. The surface topography and the thickness of the films were determined by both atomic force microscopy (AFM) and scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the \(\rho - T\) curves of these two films. The \(T_c\) is 38.1 K (\(\Delta T = 1\) K) and 34.5 K (\(\Delta T = 3\) K) for the \textit{ex situ} and \textit{in situ} annealed films respectively. The \textit{ex situ} annealed film has a higher \(T_c\) and a narrower transition width in the \(\rho - T\) curves. However, we notice that the bulk diamagnetism transition in the M-T curve for the \textit{in situ} film (\(\Delta T = 5\) K) is actually sharper than for the \textit{ex situ} annealed film (\(\Delta T = 9\) K), which indicates a more homogeneous superconducting phase in the \textit{in situ} film, as shown in the right hand inset of Fig. 1. Also shown in Fig. 1, the resistivity value of the \textit{in situ} annealed film is quite high, \(\sim 120 \mu\Omega \cdot \text{cm}\) at 300 K, whereas the value for the \textit{ex situ} film is as low as 36 \(\mu\Omega \cdot \text{cm}\). The values of the resistivity difference, \(\Delta\rho_{300\sim40}\), are both 19 \(\mu\Omega \cdot \text{cm}\) for the two films. Since the transport property for an MgB2 sample is probably governed by both intra-grain scattering and inter-grain connectivity [12], [13], it is difficult to distinguish these two aspects of the influences only from the \(\rho - T\) curves. From a comparison of the \(\rho - T\) curves of our \textit{ex situ} annealed film and a clean MgB2 single crystal [14], the \(\Delta\rho_{300\sim40}\) of our film is about five times the value for the single crystals. If we attribute the increase of \(\Delta\rho_{300\sim40}\) to a reduction of effective current carrying area by five fold, the “real” residual resistivity of our \textit{ex situ} film should be 3.4 \(\mu\Omega \cdot \text{cm}\), not too far from the residual resistivity value of about 1 \(\mu\Omega \cdot \text{cm}\) for single crystals [14], which indicates that the \textit{ex situ} film is fairly clean inside the MgB2 grains.

The stronger intra-grain scattering for the \textit{in situ} film is revealed by the \(H_a - T\) curves for the two films shown in Fig. 2. The applied field is perpendicular to the surface of the film. Since both films do not present a grain orientation according to the AFM observation [10], the comparison of \(H_{c2}\) between the two films can be reliable in revealing the difference in scattering level. The slope of \(H_{c2} - T\) for our \textit{in situ} film is about 1.1 T/K in the temperature range from 25 K to 30 K. Employing a simple linear extrapolation, which is usually applicable for dirty MgB2 samples [15], the \(H_{c2}\) value at 0 T is estimated to be as high as 36 T. This value is significantly higher than the values of \(H_{c2}(0) = 21\) T and \(H_{c2}(0) = 7.3\) T for the clean MgB2 single crystals [14], indicating a very strong scattering in our \textit{in situ} film. The \textit{ex situ} film shows a low \(H_{c2}\) slope of 0.46 T/K, attributable to a lack of intra-grain scattering, which implies that the impurity precipitates and other disorders inside the \textit{ex situ} film are at a low level.

The field dependence of \(J_c\) of the two films is shown in Fig. 3. The \(J_c\) value of the \textit{ex situ} film is higher than the \textit{in situ} film, but decreases sharply with the increasing fields. Our best \textit{in situ} annealed MgB2 film shows a weak field dependence of \(J_c\), suggesting good pinning in high fields. The \(J_c\) of the \textit{in situ} film at 5 K and 5 T remains about \(10^6\) A/cm², whereas the \(J_c\) for the \textit{ex situ} film drops to less than \(10^4\) A/cm² in the same field and temperature. The \(J_c\) behavior of the \textit{ex situ} annealed MgB2...
film is very similar to that of clean MgB$_2$ bulks, which lack flux pinning in high fields.

The MO images in Fig. 4 show some interesting differences in flux penetration behavior. The images correspond to a map of the out-of-plane component of the local magnetic field. The brighter the area, the stronger is the magnetic flux. At 4 K, the magnetic flux penetrates both films by abrupt avalanches. The in situ film shows a parallel penetration pattern from each edge of the sample, while the ex situ film shows a dendritic penetration. Upon inspection of Fig. 4, we find that the penetration paths in the in situ film are nonrepeatable in different sets of measurements. In contrast, the dendrites for the ex situ film is nearly identical for different set of measurements, although the development rate of each path may vary. The nonrepeatable flux avalanche at low temperature for the in situ film is characteristic of MgB$_2$ films, corresponding to thermo-magnetic instability [16]. The fact that flux penetrates the in situ film much further than the ex situ film in a same field implies an easier local heat-up for the in situ film, which could be attributable to a small thermal conductivity of the in situ film. The penetration behavior of the ex situ film resembles that observed in superconductors with microscopic defects, indicating defect-controlled flux jumps in the ex situ film. An explanation for the interesting differences found in MO observation may link the microstructural characteristics of the films to their superconducting properties.

Fig. 5 shows an AFM 3D image of the ex situ annealed MgB$_2$ film. Since the ex situ film has undergone a much higher annealing temperature and longer annealing time, it is reasonable to see strong crystallization after the annealing. During the grain coarsening process, the movement of the grain boundaries probably expels the disorder, such as vacancies, dislocations, impurity atoms or precipitates, from the matrix to the grain boundaries. According to the two-band phonon-mediated superconductivity revealed in MgB$_2$, the orthogonality of the electron orbitals in the two bands of MgB$_2$ suppresses inter-band scattering, but only the inter-band scattering has a pair-breaking effect in the two-band superconductor [12]. Intra-grain scattering usually increases the slope of $H_{c2}$ (T) and provides flux pinning, while makes little suppression of the $T_c$. Thus the relatively clean MgB$_2$ grains in our ex situ film might lead to the poor $J_c$ and $H_{c2}$ performance. Klie et al. have observed the presence of BOx – MgO$_y$ – BOx secondary phase along grain-boundaries in MgB$_2$ bulk samples [17]. In some peculiar positions, such as where three big MgB$_2$ grains meet together, the impurities are particularly likely to concentrate, and microscopic pores could also develop at the triple junction and act as a source of cracks. Such positions are usually the thinnest part of the film as can be seen from the AFM image in Fig. 5. These thinner, nonsuperconducting, or lower $T_c$ parts in the film may act as a preferred path for the flux penetration shown in Fig. 4(c) and (d).

Fig. 6 shows TEM and SAD pattern for the in situ MgB$_2$ film. A small-grain feature is clearly revealed by both the bright field(BF) image and the SAD ring patterns. The grain size is about 20–30 nm judging from the BF image. Strong diffraction rings from MgO also appear in the SAD image, indicating a
significant amount of MgO phase exists in the film. With the in situ preparation, the precursor film is deposited from a stoichiometric MgB$_{2}$ target. Thus the Mg and B atoms or clusters are finely mixed together in the precursor. The fine mixture, in turn, favors rapid MgB$_{2}$ phase formation. During the short annealing process, namely a 12 min ramping up process and a 1 min dwell at 685$^\circ$C, a superconducting MgB$_{2}$ phase was formed, but a long-range diffusion is unlikely. Large amounts of disorders are probably still in their initial positions, which should be finely dispersed in the film, leading to enhanced intra-grain scattering and flux pinning, as well as an increased residual resistivity and a small thermal conductivity. The observed nano-grain structure is usually found in this type of film [6], [9]. As suggested by Bugoslavsky et al., the finely distributed grain boundaries could also serve as effective pinning centers [18]. Considerable oxygen may be brought into the precursor due to magnesium’s high reactivity with oxygen [2], [10]. Upon a closer look at the SAD pattern in Fig. 6, we find that the rings from MgO are constructed with distinguishable diffraction spots, while the rings from MgB$_{2}$ are more continuous, which usually indicates a larger grain size of MgO. These large MgO grains, therefore, can barely contribute to the pinning enhancement in our in situ film due to their unfavorable size. However, further TEM study on the distribution of oxygen with the aid of Z-contrast scanning transmission electron microscopy (STEM) and convergent-beam electron diffraction (CBED) is still necessary to clarify the role of oxygen in the in situ films.

IV. CONCLUSIONS

The small-grain and high-level-disorder feature of the in situ annealed film, which is attributable to the low annealing temperature and short annealing time, may mainly contribute to the significant improvement of flux pinning in the in situ MgB$_{2}$ film. In contrast, our randomly oriented ex situ film is probably constructed of comparatively clean grains with weak links between the grains, as a result of the annealing process which is in the grain-growing region. In accordance, defect-controlled flux jump was observed by MO imaging in our ex situ annealed MgB$_{2}$ film. A low temperature quick MgB$_{2}$ phase formation could be beneficial for maintaining disorder in the film, and thus of importance for high performance MgB$_{2}$ film preparation.

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