Multi transitions in MgB\(_2\) films
prepared by pulsed laser deposition

Yi Zhao*, Yuemeng Chi, Ruijuan Nie, Furen Wang

State Key Laboratory for Mesoscopic Physics,
School of Physics, Peking University, Beijing, 100871

Abstract

We have grown MgB\(_2\) films in a postannealing process. Precursors were prepared on Al\(_2\)O\(_3\)(0001) substrates by codeposition of Mg and MgB\(_2\) using pulsed laser deposition technique. Superconducting MgB\(_2\) thin films were obtained via an \textit{ex situ} postannealing process, with various annealing temperatures and durations. In magnetic measurement we found more than one transitions in almost all the samples, and the temperature dependence of the resistance confirmed this phenomena.

*Email Address: yzhao@physics.utoronto.ca (Yi Zhao)
We proved this is not result of magnesium deficiency. Transportation properties of MgB\textsubscript{2} thin films under strong magnetic fields are also studied.

\textit{Key words:} superconducting, MgB\textsubscript{2}, film, annealing

\textit{PACC:} 6855, 7470L, 7475, 8115I

1 Introduction

The discovery of superconductivity in MgB\textsubscript{2} compound [1], with the highest transition temperature around 40K[2][3], has aroused great interest on investigating the properties of this promising material. The strongly linked nature of the inter-grains[4] with high charge carrier density and the relatively simple structure[5][6] of this material reveals its perspective for use in technological applications. Moreover, as a two-band superconductor, its simple crystal structure and high $T_c$ make it a perfect and real system to study the fundamental properties of two-band superconductivity[7][8].

There are two approaches of the postannealing technique: the \textit{in situ} method and the \textit{ex situ} method. The \textit{in situ} process is more compact and more likely to grow smooth films, however, this way of growth has several disadvantages, like poor crystallinity, multiphase, and relatively low $T_c$[9][10].
Ex situ methods are exploited to overcome both of the two essential factors for the fabrication of superconducting MgB$_2$ thin films: the vapor pressure of magnesium and the oxidation of magnesium, and have achieved films with quite high $T_c$ and $J_c$\cite{11}\cite{12}. Recently the ex situ approach has been greatly improved. As an essential part of superconductor device, Josephson junction has been fabricated on ex situ grown MgB$_2$ thin films\cite{13}.

In this paper, we report the superconducting properties, including some unusual phenomena, of MgB$_2$ thin films fabricated under various annealing temperatures and durations. In magnetic measurement we found more than one transitions in almost all the samples, and the temperature dependence of resistance confirmed this phenomena. We compared our results with some other groups’ works, and proved a different explanation. We also studied the transportation properties of samples under different magnetic fields, extracting their upper critical fields.

2 Experimental

The MgB$_2$ thin films used in this study were prepared in an ex situ postannealing approach: the precursors were all prepared on Al$_2$O$_3$(0001) sub-
strates by codeposition of high purity Mg and MgB$_2$ targets at room temperature using pulsed laser deposition technique in a high vacuum condition of $\sim 1.5 \times 10^{-7}$ Torr. The laser energy and pulse repetition rate were 700mJ/pulse and 8 Hz, respectively. An additional Mg layer was deposited as a cap on the precursor immediately after codeposition. The precursors were black with metal luster, and darkened after being exposed to the air for a few days, which is believed to be the oxidation of magnesium coat.

After deposition, the precursors were put in a sealed Ta tube and annealed in Mg atmosphere. The annealing temperatures were 600°C, 700°C, 800°C, 900°C and 1000°C, respectively. The durations of the annealing process were 10min, 20min, 40min and 60min, respectively. Pure argon was flowing around the samples during the thermal treatment. Enough magnesium tapes were applied to keep a high Mg vapor pressure. Special measures were taken to make sure that the magnesium tapes would not contact the surface of samples directly. The samples after annealing were either golden or black.

The magnetization versus temperature measurements were performed using standard SQUID magnetometer device (quantum design MPMS). Sample was first cooled to 5K in zero field, then a low magnetic field of 50Oe was utilized in the direction parallel to the surface of the sample. The sample was
then heated to 50K in this field. The magnetization of sample was measured every 1K after the stabilization of system temperature. Measurements of magnetic properties were performed on all samples.

We obtain the temperature dependence of resistance using a quantum design PPMS (Physical Properties Measurement System) device. A classical four-probe approach was applied. We measured the resistances of samples in the magnetic fields of 0T, 0.5T, 1T, 2T, 4T, 6T and 8T, respectively, in the direction perpendicular to the surface of the sample. Once the sample reached 50K, when it had transferred from superconducting state to normal state completely, the magnetic field was removed, and the sample was cooled in zero field again to measure its resistance under another magnetic field.

ICP (Inductively Coupled Plasma Spectrometry) measurement was also performed on several samples to obtain molar ratio of magnesium to boron. To avoid the influence of extra magnesium attached to the edge of the substrate, we carefully scratched the film from the substrate to nitric acid in which the powder dissolved.
3 Results and discussion

The precursors were all around 2000Å thick, including the Mg cap of around 180Å. After annealing, the thin films were around 4000Å thick. The reason why the thin film thickened after annealing can be explained as the result of epitaxial growth, the oxidation of the magnesium cap, etc. However, these explanations are not sufficient. We are still seeking for the reason.

In magnetic measurement, we found the temperature dependence of magnetization of most samples contains two transitions, as shown in figure 1 and figure 2. The distribution of transition temperatures is not random but concentrates in several certain temperatures: most of them have a magnetization drop at around 38K, which is weaker compared to another magnetization drop at around 20K. In figure 2 we can see the transition temperature of sample 600C40M is 22K. However, it has a secondary transition at 8K, which is exactly the transition temperature of sample 600C20M. As a typical two-transition sample, full chart of 700C60M is presented in figure 2. We can observe its two transitions clearly, and from the value of diamagnetization we can infer the superconductivity of 38K-\( T_c \) compositions is much weaker than that of 22K-\( T_c \) compositions. Both 700C40M and 900C10M have high transition temperatures. Actually 900C10M has a little magnetization drop
at 36K before its primary transition at 33K, as the inset of figure 2 shows. The uniform existence of more than one magnetization transitions indicates that these thin films contain several superconducting compositions with different critical temperatures. Table 1 summarized the magnetic measurement results.

More than one transitions in magnetic measurement is also reported in the works of Shinde et al. [14] and Ivanov et al. [10]. Despite the common transition at 39K, Shinde et al. reported transitions at 22K and 8K, while Ivanov et al. reported transition at around 20K. They explained this phenomena as the deficiency of magnesium, which led to the formation of MgB$_4$, MgB$_6$, etc. However, according to our results of ICP analysis (Table 2), all samples were excessively Mg-riched. Therefore the deficiency of magnesium may not be able to explain the secondary transition. To the contrary, sample 800C20M, which has the lowest Mg-B molar ratio, showed the strongest diamagnetization around 38K among all samples analyzed in ICP. Moreover, the temperature dependence of the resistance of 800C20M (figure 3) and 900C20M (figure 5) shows the former one has much stronger superconductivity than the latter one, which shows the highest Mg-B molar ratio in ICP analysis.
The temperature dependence of the resistance of sample 800C20M, 900C10M, 900C20M and 1000C10M are shown in figure 3, 4, 5 and 6 respectively. Strong magnetic field has obvious effect to suppress the transition temperature, which is also reported by others’ works[15][16][17]. Sample 900C10M has the highest zero resistance temperature under any field, while sample 900C20M has the lowest. Sample 1000C10M has the similar zero resistance temperature as sample 900C20M does in low field. However, strong magnetic field has greater effect on sample 900C20M than that on sample 1000C10M.

We can see that the zero resistance temperatures of the samples under zero field are consistent with their lower transition temperatures, not the upper ones, of their magnetic measurement results. However, we can observe that the resistances start to fall at around 38K under zero field, which matches their upper transition temperatures, in the insets of figure 3, 5 and 6. Considering the upper transitions at around 38K in the results of magnetic measurement, the only explanation to this fall is that some compositions of the thin film turned to be superconducting under 38K, leading to local short circuit and reduced the whole resistance. According to the diamagnetization (see 700C60M in figure 2), only few superconducting compositions have a $T_c$ of 38K. These high-$T_c$ compositions are probable large superconducting
grains spread in some local areas of the film. The low zero resistance temperature shows these high-$T_c$ compounds are not topologically connected, so the resistance just falls, not disappears at around 38K, although the sample has already shown a diamagnetization. The sample turns to be completely superconducting only after its lower transition, when most of its compositions turn to be superconducting.

The magnetic field we utilized in magnetic measurement is on the different direction to that we utilized in resistance measurement, but it does not weaken our comparison above. The magnetic field we utilized in magnetic measurement was very low, and would have little influence to the superconductivity of the film. Meanwhile the temperature dependence of resistance we used for comparison was obtained under zero field. Results of both measurements reflected the inner properties of the sample, not the interaction between the sample and the external magnetic field. Therefore the difference direction of magnetic fields is not a problem here.

M. Rajteri et al explained such existence of two transitions as "a diphasic percolation process" [18]. It was reasonable but a bit too simple. To give more detailed explanations, we noticed the crystal lattice mismatch between the sapphire substrate and the MgB$_2$ film on it. Such mismatch has remarkable
influence on the film, especially for the bottom layer of the film\textsuperscript{19}. We have reason to believe the mismatch lead to the lattice distortion of the bottom layer of the film. Because density of states at $E_F$ of MgB$_2$ is very sensitive to the lattice parameters\textsuperscript{20}, the change of lattice parameters will affect the superconductivity of the bottom layer greatly. We conclude that the transition temperature of the bottom layer is different from that of the top layer, leading to multi transitions. However, this is just a theoretical analysis and we do not have direct supportive evidence, like SEM photo or XRD. We are working to find out the exact substance of the low-$T_c$ compositions.

The discrepancy between temperature dependence of resistance and temperature dependence of magnetization is not only reported in our study. They are reported to be consistent in many works\textsuperscript{21, 22, 23}. In the work of W. N. Kang \textit{et al}\textsuperscript{12}, however, all their samples showed a $T_c$ around 38K in resistive measurement, while most samples showed a significant magnetization drop far below 38K in their magnetic measurement. They did not give a detailed show of temperature dependence of magnetization, but from their resistance measurement we can infer that their samples all contained a few compounds with $T_c$ around 38K. Different from our samples, such compounds in theirs must have connected topologically so that the resistance disappeared before
a significant drop of magnetization.

We believe the discrepancy between temperature dependence of resistance and temperature dependence of magnetization is the result of competition of superconducting compounds with different critical temperatures. If the high-$T_c$ compounds have connected topologically, the resistance turns to be zero before a significant drop of magnetization, otherwise the resistance will still exist when a diamagnetization is shown.

Multi transitions has never been reported in the papers of high quality MgB$_2$ films, because the singularity of high-$T_c$ compound covered properties of other compounds. Our samples, although were not of best quality, provide a perfect opportunity to investigate some basic physical characteristics of this material.

Another noticeable phenomena in the temperature dependence of resistance is the systematically sharp increase of resistance just above the transition temperature. This cannot be explained as the overshoot of current because more than one minute would be cost to stabilize the system temperature, in which both the current and the voltage had enough relaxation time, before the measurement of resistance was taken. In sample 800C20M such resistance peak appeared under any magnetic field (the inset of figure 3), and the field
had the effect to suppress the height of the peak. In sample 1000C10M the peak appeared under weak fields (0T and 0.5T) (the inset of figure 6), while in sample 900C20M the peak only appeared under zero field (the inset of figure 5). Sample 900C10M did not show this peak. The peak may be the result of the competition and transformation between superconductor and semiconductor compounds, but this cannot explain why the magnetic field can suppress the height of the peak. The research on this strange but systematic phenomena is undergoing.

On the basis of Ginzburg-Landau Theory, we can estimate the upper critical fields of samples based on their transition curves in different magnetic fields. Critical fields extracted are shown in figure 7 (based on the zero resistance temperature). From the figure we can estimate sample 800C20M has the highest upper critical field: 15.5T. Noticing the magnetic fields we utilized are perpendicular to the films, this is a relatively high value. Sample 900C20M has the lowest critical field: 8.8T. We noticed that sample 900C10M remains superconducting up to around 20K in magnetic field of 8T, revealing its capability to work under strong magnetic field at a temperature that can be easily provided by modern cryocooler. We also extracted the critical fields from the onset temperatures of the samples, as shown in the inset of
Of course it is much higher than the critical fields extracted from zero resistance temperatures. Again sample 800C20M has the highest value: 26.2T, while 900C20M still has the lowest value: 14.8T. We have to point out this is just an approximate estimation. To estimate more strictly, two-band G-L theory should be utilized\[25\].

4 Summary

Precursors were prepared on Al$_2$O$_3$(0001) substrates by codeposition of Mg and MgB$_2$ targets using pulsed laser deposition technique. Superconducting MgB$_2$ thin films were obtained via an \textit{ex situ} postannealing process, with various annealing temperatures and durations. The superconducting properties of the samples were intensively investigated. In magnetic measurement, more than one transitions appeared in almost all the samples, suggesting these films contained several superconducting compounds. The temperature dependence of resistance confirmed this phenomena. The ICP analysis proved this is not result of magnesium deficiency. We believe the resistively measured critical temperature of MgB$_2$ thin films is determined by the competition of superconducting compounds with different critical temperatures.
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Table 1: The annealing conditions and magnetic measurement results of the samples.

(Annl.=Annealing, Temp.=Temperature, U.=Upper, L.=Lower, Trans.=Transition)

| Sample ID | Annl. Temp. | Annl. Time | U. Trans. Temp. | L. Trans. Temp. |
|-----------|-------------|------------|-----------------|-----------------|
| 600C20M   | 600°C       | 20min      | 8K              | —               |
| 600C40M   | 600°C       | 40min      | 22K             | 8K              |
| 700C20M   | 700°C       | 20min      | 38K             | 22K             |
| 700C40M   | 700°C       | 40min      | 38K             | —               |
| 700C60M   | 700°C       | 60min      | 38K             | 22K             |
| 800C20M   | 800°C       | 20min      | 38K             | 26K             |
| 800C40M   | 800°C       | 40min      | 38K             | 15K             |
| 900C10M   | 900°C       | 10min      | 36K             | 33K             |
| 900C20M   | 900°C       | 20min      | 35K             | 18K             |
| 1000C10M  | 1000°C      | 10min      | 38K             | 18K             |
| 1000C20M  | 1000°C      | 20min      | 38K             | 30K             |
| Sample ID | Concentration | Molar Ratio |
|-----------|---------------|-------------|
| 600C20M   | 2.48mg/L      | 0.332mg/L   | 3.42       |
| 700C20M   | 3.64mg/L      | 0.418mg/L   | 3.99       |
| 800C20M   | 3.66mg/L      | 0.550mg/L   | 3.05       |
| 900C20M   | 5.24mg/L      | 0.371mg/L   | 6.47       |
Figure 1: Some typical two-transition normalized temperature dependence of magnetization. All these samples have a magnetization drop at around 38K, many of them have a secondary transition around 20K.
Figure 2: Full chart for normalized temperature dependence of magnetization of several samples. Two transitions in sample 600C40M and 700C60M can be clearly observed. A tiny secondary transition of sample 900C10M is also shown in the inset.
Figure 3: Temperature dependence of the resistivity under different magnetic fields for sample 800C20M.
Figure 4: Temperature dependence of the resistivity under different magnetic fields for sample 900C10M.
Figure 5: Transition curves in different magnetic fields for sample 900C20M.
Figure 6: Transition curves in different magnetic fields for sample 1000C10M.
Figure 7: Critical field based on zero resistance temperature. The magnetic field is perpendicular to the surface of the films. Critical field based on onset temperature is presented in the inset.