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2005

## Fabrication and characterization of superconducting PLD MgB<sub>2</sub> thin films

Yue Zhao

*University of Wollongong*, yue\_zhao@uow.edu.au

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# **Fabrication and Characterization of Superconducting PLD MgB<sub>2</sub> Thin Films**

A thesis submitted in fulfillment of the  
requirements for the award of the degree

**Doctor of Philosophy**

From

**University of Wollongong**

By

**Yue Zhao, M.E.**

Institute of Superconducting & Electronic Materials  
Faculty of Engineering

2005

## **Certification**

I , Yue Zhao, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials, Faculty of Engineering, University of Wollongong, is wholly my own work unless other wise referenced or acknowledged. The document has not been submitted for any other academic institution.

Yue Zhao

16 December 2005

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## Abstract

The aim of this thesis was to study the thin film of magnesium diboride ( $\text{MgB}_2$ ) superconductor based on PLD synthesis technique. The  $\text{MgB}_2$  is a very simple binary compound with a number of surprising properties. The discovery of superconductivity with a critical temperature ( $T_c$ ) of 39 K in bulk  $\text{MgB}_2$  in January 2001 has attracted a huge research interests worldwide in this material. In a hope to substitute  $\text{MgB}_2$  superconducting electronics for low temperature superconducting electronics and compete with high temperature superconductors, the preparation techniques of  $\text{MgB}_2$  thin films need to be advanced from a material engineering point of view. On the other hand, new studies regarding the different behaviours of  $\text{MgB}_2$  thin films and  $\text{MgB}_2$  bulks will assist the scientific community to better understand the physics in this superconductor.

We began the study with *in situ*  $\text{MgB}_2$  film preparation using normal on-axis geometry. The *in situ* annealing conditions of pulsed laser deposited  $\text{MgB}_2$  films were studied. We found that the superconducting properties depend in a crucial way on the annealing conditions: temperature, heating rate and time. We tested the  $T_c$  dependence of the *in situ* annealed  $\text{MgB}_2$  films by changing various process parameters, including laser energy density, target-substrate distance, background gas, annealing temperatures, heating rates and dwell times. The film processing conditions were optimized and good quality *in situ* films were obtained routinely, with good reproducibility. The hysteresis loops of magnetic moment versus applied field at different temperatures indicate a weak field dependence in high fields. Magneto-optical imaging of the films showed quite homogeneous magnetic flux penetration, indicating structural homogeneity. The films without annealing show no superconductivity.

Another method using *ex situ* annealing has also been tested for a better crystallization of the  $\text{MgB}_2$  film, as well as for reference purposes. In the *ex situ* annealing process, we first deposited boron precursor film on a sapphire substrate and then wrapped it in Ta foil and sealed it in a stainless steel tube together with pure Mg pellets, under protective Ar atmosphere. The tube was then annealed in tube furnace and kept at 900°C for 30 min. With this method, we obtained *ex-situ*  $\text{MgB}_2$  films of comparable quality as those reported so far in the literature, and used them as a benchmark to test possible improvements in  $\text{MgB}_2$  thin film technology based on PLD.

Significant differences in properties between the *in situ* films and *ex situ* films were found. The *ex situ* annealed  $\text{MgB}_2$  film has a  $T_{c \text{ onset}}$  of 38.1K, while the *in situ* film has a suppressed  $T_{c \text{ onset}}$  of 34.5K. The resistivity at 40K for the *in situ* film is larger than that of the *ex situ* film by a factor of 6. The residual resistivity ratios are 1.1 and 2.1 for the *in situ* and *ex situ* films respectively. The field dependence of the resistivity-temperature curves has been measured. A large slope of the  $H_{c2}$ -T curve was obtained for the *in situ* annealed film. The  $J_c$ -H curves of the *in situ* film show a much weaker field dependence than those of the *ex situ* film, attributable to stronger flux pinning in the *in situ* film. The microstructural differences between the two types of films are observed by AFM and TEM. The small-grain (<60nm) size and a high oxygen level detected in the *in situ* annealed  $\text{MgB}_2$  films may be decisive for the significant improvement of  $J_c$  and  $H_{c2}$ .

In order to enhance the performance of the  $\text{MgB}_2$  films, various amounts of Si up to a level of 18wt% were added into  $\text{MgB}_2$  thin films fabricated by pulsed laser deposition. Si was introduced into the PLD  $\text{MgB}_2$  films by sequential ablation of a stoichiometric  $\text{MgB}_2$  target and a Si target. The  $T_c$ 's of the Si added  $\text{MgB}_2$  thin films

were tested. A  $J_c$  enhancement was observed in the Si added  $MgB_2$  films. For the ~3.5wt% Si addition, the best enhancement circumstance, the magnetic critical current density ( $J_c$ ) of the film at 5K was increased by 50% as compared to the undoped film. The slope of  $H_{irr}(T)$  and  $H_{c2}(T)$  curves of the 3.5wt% Si added  $MgB_2$  film was slightly higher than that for the undoped film.

For the application in superconducting electronics, the surface smoothness of the  $MgB_2$  thin film is of crucial importance. We pioneered an off-axis deposition geometry in the PLD  $MgB_2$  films preparation. Highly smooth and  $c$ -axis oriented superconducting  $MgB_2$  thin films were successfully achieved with a off-axis geometry. The films were deposited on  $Al_2O_3$ -C substrates, aligned perpendicular to a stoichiometric  $MgB_2$  target in a 120 mTorr high purity Ar background gas. An *in situ* annealing was carried out at 650°C for 1 min in a 760 Torr Ar atmosphere. Despite the short annealing time, an x-ray  $\theta$ -2 $\theta$  scan shows fairly good crystallization, according to the clear  $c$ -axis oriented peaks for the films. Both atomic force microscopy and the x-ray diffraction results indicated that the crystallite size is less than 50nm. The root mean square roughness of our off-axis film was ~4 nm in a  $5 \times 5 \mu m^2$  area. The zero resistance  $T_c$  value of the best off-axis film reached 32.2 K with a narrow transition width of 0.9 K. The films showed no anisotropy in  $H_{c2}$ - $T$  curves when parallel and perpendicular fields were applied relative to the film surface. The slope of  $H_{c2}$ - $T$  curves is ~1 T/K, which is still among the highest reported values.

On the basis of successful preparation of smooth off-axis  $MgB_2$  films, we obtained  $MgB_2/Mg_2Si$  multilayer structure by sequentially switching a stoichiometric  $MgB_2$  target and a Si target during off-axis pulsed-laser deposition. The transmission electron microscope cross-sectional image of the resulting film exhibits a layered structure with each  $MgB_2$  layer being 40-50 nm thick and the  $Mg_2Si$  inter-layers about

5 nm thick. A clear enhanced anisotropy in the irreversibility lines and the vortex activation energy was observed. Pinning and the flux flow activation energy for this type of film was significantly increased in parallel applied fields.

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**Fig.4-8** Irreversibility lines and upper critical field versus temperature curves for the in situ and ex situ annealed films. A): Irreversibility lines for the in situ and ex situ films. The data for undoped ex situ  $\text{MgB}_2$  film and oxygen alloyed  $\text{MgB}_2$  film (Ref. [2]) is displayed in the figure for comparison. B): Upper critical fields versus temperature for the two films. The data for c-axis-oriented  $\text{MgB}_2$  films from Ref. [3] are also shown in this figure.

**Fig.4-9** Critical current of the two types of  $\text{MgB}_2$  films calculated from M-H loops.

Solid symbols: in situ annealed film; lines: ex situ annealed film. The temperature is 5 K, 10 K, 15 K, and 20 K from top to bottom, respectively. The applied field is perpendicular to the film plane.

**Fig.4-10** MO images for the in situ film, shown in (a), (b) and the ex situ film, shown in (c), (d) at 4 K. The applied field is (a) 17 mT, 1<sup>st</sup> set of measurement, (b) 17 mT, 2<sup>nd</sup> set of measurement, (c) 25.5 mT, 1<sup>st</sup> set of measurement, and (d) 25.5 mT, 2<sup>nd</sup> set of measurement.

**Fig.4-11** AFM of a) the in situ and b) the ex-situ MgB<sub>2</sub> film on Al<sub>2</sub>O<sub>3</sub>-Rsubstrate.

**Fig.4-12** EDS analysis results for the a) in situ and b) ex situ films. In order to avoid the interaction with the Al<sub>2</sub>O<sub>3</sub> substrate, a low electron beam energy of 5kV was used. As a result, no Al signal at about 1.5 KV is detectable. Since the thickness of both films is similar, the difference in oxygen signal intensity can reveal the difference of oxygen level in the two films.

**Fig.4-13** AFM 3D image of the ex situ MgB<sub>2</sub> film. The surface topography shows typical randomly oriented grains. The arrow shows a thinner part formed between two grains.

**Fig.5-1** AFM deflection image of Si islands on sapphire-R substrate deposited for 50 pulses (10Hz, 5sec). The laser fluence is 300mJ/pulse.

**Fig.5-2** EDS Si mapping in the Si doped MgB<sub>2</sub> films. The upper part contains SEM secondary electron images, and the lower part the distribution of Si. a: 3.5% Si addition, b: 11% Si addition. The arrows indicate the Si-rich spots.

**Fig.5-3** DC magnetization curves of the films with different Si doping levels. The applied field is 25 Oe for both ZFC and FC measurements.

**Fig.5-4** J<sub>c</sub> values with different Si doping levels. a: at 5 K, b: at 10 K, c: at 15 K. The applied field B<sub>a</sub> is perpendicular to the film plane.

**Fig.5-5** Irreversibility lines and upper critical fields of the 3.5% Si doped and undoped MgB<sub>2</sub> films.

**Fig.5-6** The resistivity versus temperature curves in fields from 0T to 8.7T. a: undoped film; b: 3.5wt% Si film; c: 5wt% Si film.

**Fig.5-7** The  $J_c$  and  $\rho_{40K}$  versus Si addition level in the doped films. The solid squares represent the magnetic  $J_c$  at 5K and 1.5T. The open circles represent residual resistivity  $\rho_{40K}$ .

**Fig.6-1** Illustration of on axis deposition and off-axis deposition.

**Fig.6-2** Kennedy 's design of the off-axis deposition of smooth YBCO film.

**Fig.6-3** Schematic Illustration of the off-axis deposition geometry for MgB<sub>2</sub> thin film deposition.

**Fig.6-4** SEM cross-sectional images of four films on Al<sub>2</sub>O<sub>3</sub> –C substrates using different deposition conditions, namely (a): on-axis deposition, laser energy flux = 300 mJ/pulse, laser repetition frequency = 10 Hz, growth rate=12 Å/sec; (b) off-axis, E=500mJ/pulse, F=10Hz, 16Å/sec; (c) off-axis, E=300mJ/pulse, F=10Hz, 4 Å/sec; and (d) shaded off-axis, E=500mJ/pulse, F=5Hz, 2 Å/sec. The scale is the same for all four images.

**Fig.6-5** The ZFC magnetization curves for the off-axis MgB<sub>2</sub> films prepared with different annealing temperatures. The substrate temperature during deposition is 250°C for all the samples. The ramp time from 250°C to the annealing temperature is 12 min and the dwell time is 1min.

**Fig.6-6** ZFC magnetization curves of off-axis MgB<sub>2</sub> films deposited on different substrate temperatures. The in situ annealing condition is the same as above-mentioned optimized parameters.

**Fig.6-7**  $T_{c \text{ onset}}$  versus  $T_{\text{substrate}}$  curve (left axis) and Magnetization (right axis) versus  $T_{\text{substrate}}$  at 5K. The  $T_c$  and Magnetization values are extracted from ZFC magnetization curves at 5 K in Fig.6-6.

**Fig.6-8** AFM deflection image of a  $2 \times 2 \mu\text{m}^2$  area of the surface of film (d) in Fig.6-4.

**Fig.6-9** AFM cross-section profile of the off-axis film #300604V. The vertical distance between the highest and the lowest part indicated by arrows is 22nm.

**Fig.6-10** XRD  $\theta$ -2 $\theta$  pattern of the off-axis deposited film #300604V with a slow scanning rate of 0.2 degree/min. The vertical lines label the positions for all  $\text{MgB}_2$  peaks in powder diffraction database. The unknown peak at  $37.56^\circ$  is also presents in the spectrum of a bare  $\text{Al}_2\text{O}_3$ -C substrate, so we assume it is not from the film.

**Fig.6-11** The left figure: Bright field TEM image of a planar specimen a typical off-axis  $\text{MgB}_2$  film with a zero-resistivity  $T_c$  of 32K. The right figure is a SAD pattern from a  $\Phi 500 \text{ nm}$  area of the film

**Fig.6-12** Resistivity versus temperature for an off-axis film #300604V. The inset is an enlargement of the transition part.

**Fig.6-13** The field dependence of resistivity-temperature curves of the off-axis  $\text{MgB}_2$  film #300604V in a) perpendicular ( $H//c$  axis) fields and b) parallel fields ( $H//a$ -b plane).

**Fig.6-14** The Arrhenius plot of resistance  $R(T, H)$  for the off-axis  $\text{MgB}_2$  film in a) perpendicular and b) parallel fields.

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**Fig.6-16** The  $H_{c2}$ -T curves for  $H \parallel ab$ -plane and  $H \perp ab$ -plane. The  $H_{c2}$  values are derived from transport curves using 90%  $\rho_{Tc}$  values. In both  $H \parallel ab$ -plane and  $H \perp ab$ -plane cases, the testing current was perpendicular to the applied field.

**Fig.6-17** Magnetic  $J_c$  versus applied field for the off-axis film #300604V at different temperatures. The applied field is perpendicular to the film plane. It is difficult to estimate  $J_c$  at 5 T in low fields owing to the predominant magneto-thermal instability.

**Fig.6-18** MOI of an typical off-axis  $MgB_2$  film with a zero-resistivity  $T_c$  of 32K.

Fig.6-19 MOI of the on-axis  $MgB_2$  film #030703 (a) 4K 3.4 mT (b) 4K 8.5 mT (c) 4K 25.5 mT; (d) 7.5K, 5.1mT (e) 7.5K, 10.2 mT (f)7.5K, 17 mT; (g)15K, 3.4 mT (h)15K, 10.2mT (i)15 K, 27.2 mT.

**Fig.6-20** MOI image details of a) on-axis film 7.5K 10.5mT, and b) off-axis film at 7K 14.2 mT.

**Fig.7-1** Cross-sectional SEM image of the multilayer film. The inset is a BF TEM image of the multilayer film.

**Fig.7-2** TEM BF image of the multilayer film. The scale bar is 100 nm. The inset is an SAED of the  $MgB_2$  film, showing a clear textured grain orientation.

**Fig.7-3** Resistivity versus temperature curves of multilayer film and  $MgB_2$  film.

**Fig.7-4** Resistivity versus temperature curves of a multilayer film in: a) perpendicular fields; b) in parallel fields.

**Fig.7-5** The  $H_{c2}$  versus  $T/T_c$  for the multilayered film and  $MgB_2$  film.

**Fig.7-6** The irreversibility fields of the multilayer film and the  $MgB_2$  film.

**Fig.7-7** The Arrhenius plot of resistance  $R(T, H)$  for the multilayer film in: a) perpendicular and b) parallel fields.



**Fig.7-8** The activation energy,  $U_0$  of flux flow versus applied field,  $B_a$ .

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**Table 3-1**  $T_c$  values of  $\text{MgB}_2$  films versus laser energy and target-substrate distance,  $D_{\text{T-S}}$ .

**Table 5-1** Si content and corresponding  $T_c$  in the in situ annealed  $\text{MgB}_2$  films produced by PLD.

### **List of Publications during PhD study period (from 2002 to 2005)**

1. **Y. Zhao**, S. X. Dou M. Ionescu P. Munroe, “Significant improvement of activation energy in the MgB<sub>2</sub>/Mg<sub>2</sub>Si multilayer film”, accepted by Appl. Phys. Lett., To be published in Feb. 2006
2. **Y. Zhao**, S. X. Dou M. Ionescu P. Munroe, “Transport properties of multilayered MgB<sub>2</sub>/Mg<sub>2</sub>Si superconducting thin film” accepted by J. Appl. Phys. To be published in Jun 2006
3. **Y. Zhao**, M. Ionescu, M. Roussel, a. V. Pan, J. Horvat, and S. X. Dou, “Superconducting and microstructural properties of two types of MgB<sub>2</sub> films prepared by pulsed laser deposition, IEEE Transactions on Applied Superconductivity” **15**, 3261 (2005).
4. **Y. Zhao**, M. Ionescu, J. Horvat and S. X. Dou, “Off-axis MgB<sub>2</sub> films using an *in situ* annealing pulsed laser deposition method”, Supercond. Sci. & Technol. **18**, 395-399 (2005)
5. S. X. Dou, S Soltanian, **Y. Zhao**, E Getin, Z Chen, O. Shcherbakova and J. Horvat “The effect of nanoscale Fe doping on the superconducting properties of MgB<sub>2</sub>” Supercond. Sci. Technol. **18**, 710 (2005)
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7. **Y. Zhao**, M. Ionescu, J. Horvat and S.X. Dou “Comparative study of *in situ* and *ex situ* MgB<sub>2</sub> films prepared by pulsed laser deposition” Supercond. Science & Technology **17**, S482-S485 (2004)

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9. M. Ionescu, **Y. Zhao**, M. Roussel, S.X. dou, R. Ramer and M. Tomsic “Flux pinning in MgB<sub>2</sub> thin films grown by pulsed laser deposition” Journal of Optoelectronics and Advanced Materials, **6**, 169-176 (2004)
10. A.V. Pan, **Y. Zhao**, M. Ionescu, S.X. Dou, V.A. Komashko, V.S. Flis, and V.M. Pan, "Thermally activated depinning of individual vortices in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> superconducting films", *Physica C*, **407**, 10 (2004)
11. M. Ionescu, A. H. Li, **Y. Zhao**, H. K. Liu, A. Crisan, "Enhancement of critical current density in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-d</sub> thin films grown by PLD on YSZ (001) surface modified with Ag nano-dots", J. Phys. D: Applied Physics, **37**, 1824 (2004)
12. **Y. Zhao**, M. Ionescu, A.V. Pan, S.X. Dou and E.W. Collings “*In situ* annealing of superconducting MgB<sub>2</sub> films prepared by pulsed laser deposition” Supercond. Sci. Technol. **16**, 1487-1492 (2003)