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Fabrication and characterization of superconducting PLD MgB2 thin films

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Fabrication and Characterization of Superconducting PLD MgB_2 Thin Films

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

Doctor of Philosophy

From

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By

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Faculty of Engineering

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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 (MgB_2) superconductor based on PLD synthesis technique. The 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 MgB_2 in January 2001 has attracted a huge research interests worldwide in this material. In a hope to substitute MgB_2 superconducting electronics for low temperature superconducting electronics and compete with high temperature superconductors, the preparation techniques of 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 MgB_2 thin films and MgB_2 bulks will assist the scientific community to better understand the physics in this superconductor.

We began the study with *in situ* MgB_2 film preparation using normal on-axis geometry. The *in situ* annealing conditions of pulsed laser deposited 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 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 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 900ºC for 30 min. With this method, we obtained *ex-situ* 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 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 MgB_2 film has a $T_{c\ onset}$ of 38.1K, while the *in situ* film has a suppressed $T_{c\ onset}$ 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 MgB_2 films may be decisive for the significant improvement of J_c and H_{c2}.

In order to enhance the performance of the MgB_2 films, various amounts of Si up to a level of 18wt% were added into MgB_2 thin films fabricated by pulsed laser deposition. Si was introduced into the PLD MgB_2 films by sequential ablation of a stoichiometric MgB_2 target and a Si target. The T_c's of the Si added 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 MgB2 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℃ for 1 min in a 760 Torr Ar atmosphere. Despite the short annealing time, an x-ray θ-2θ 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 5×5 μm^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

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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_2/Mg_2Si 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_2/Mg_2Si 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_2 films prepared by pulsed laser deposition, IEEE Transactions on Applied Superconcuctivity" **15,** 3261 (2005).

4.**Y. Zhao**, M. Ionescu, J. Horvat and S. X. Dou, "Off-axis MgB_2 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_2" Supercond. Sci. Technol. **18**, 710 (2005)

6. M. Roussel, A. V. Pan, A. V. Bobyl, **Y. Zhao**, S. X. Dou, and T. H. Johansen, Magnetic flux penetration in MgB_2 thin films produced by pulsed laser deposition, Supercond. Sci. Technol. **18,** 1391 (2005).

7. **Y. Zhao**, M. Ionescu, J. Horvat and S.X. Dou "Comparative study of *in situ* and *ex situ* MgB_2 films prepared by pulsed laser deposition" Supercond. Science & Technology **17**, S482-S485 (2004)

8. **Y. Zhao**, M. Ionescu, J. Horvat, A.H. Li and S.X. Dou " Si addition in *in situ* annealed MgB_2 thin films by pulsed laser deposition" Superconductor Science & Technology **17** 1247-1252 (2004)

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11. M. Ionescu, A. H. Li, **Y. Zhao**, H. K. Liu, A. Crisan, "Enhancement of critical current density in YBa2Cu3O7-d 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_2 films prepared by pulsed laser deposition" Supercond. Sci. Technol. **16,** 1487-1492 (2003)