Local Structure Analysis of MgB₂ Thin Films by Polarized XAFS*

Mami Seo, Takafumi Miyanaga,[†] and Tomoe Kanno

Department of Advanced Physics, Hirosaki University, Hirosaki, Aomori 036-8561, Japan

Kouki Takeda, Daichi Hatanaka, and Masahito Yoshizawa

Graduate School of Engineering, Iwate University, Morioka, Iwate 020-8551, Japan

(Received 31 August 2012; Accepted 19 November 2012; Published 1 December 2012)

We analyzed the polarization-dependent XAFS of Mg *K*-edge for 10 nm, 20 nm, 30 nm and 50 nm MgB₂ films deposited by MBE method on ZnO single crystal. The structure of 30 nm MgB₂ film was similar to that for 50 nm one, even the interatomic distances for 30 nm film are slightly shorter than that for 50 nm. This indicates that the quality of 30 nm MgB₂ film is enough high as 50 nm and thicker one. On the other hand, the structures of 10 nm and 20 nm MgB₂ films were different from 30 nm and 50 nm films. The XAFS of 20 nm MgB₂ could be reproduced by the sum of that of 30 nm film and MgO, suggesting that the 20 nm MgB₂ film is mixture of hexagonal MgB₂ and MgO phase. 10 nm MgB₂ has a different structure from 20 nm nor thicker than 30 nm films.

[DOI: 10.1380/ejsnt.2012.633]

Keywords: MgB₂ film; Polarized XAFS; Mg *K*-edge; Superconductor

I. INTRODUCTION

Superconducting MgB₂ discovered in 2001 shows a transition temperature of 39 K [1], which is the highest one among metallic compounds. The superconducting mechanism and applications as a device are attracting great interest.

An important issue for the application to the device is the production of high-quality MgB₂ thin films. For this purpose, various methods of film growth have been investigated.

For the heteroepitaxial method, the interface state between MgB₂ and the substrate affects the quality of the crystal growth. Although MgB₂ thin film grown-up on ZnO forms a reactive region in their interface, its crystallinity and superconductivity performance have been improved [2]. The lattice constant of ZnO is close to that of MgB₂ (the lattice mismatch is about 5%) and therefore it is expected to be as a suitable buffer layer.

For studying the local structure of such thin films, EXAFS (extended X-ray absorption fine structure) using a synchrotron radiation source is a powerful tool. The study of MgB₂ thin film by polarized XAFS is effective, because the lattice structure of MgB₂ is hexagonal and has an anisotropic structure.

We have previously analyzed the local structure of 50 nm and 150 nm MgB₂ thin films and obtained result that they show almost same structure as MgB₂ hexagonal crystal and their structural change was significant [3]. For application of the superconducting films to the industry, to study the structure for thinner films is important.

In this paper we investigated the local structure of 10 nm, 20 nm and 30 nm MgB₂ films deposited on the O-side surface of ZnO in comparison to 50 nm MgB₂ film.

II. EXPERIMENTAL

10 nm, 20 nm and 30 nm thick MgB₂ films were prepared by a co-evaporation MBE (molecular beam epitaxy) method [4]. The MgB₂ films were deposited on the O-side of ZnO single crystal.

Mg *K*-edge (1309 eV) X-ray absorption spectra were measured on BL11A at Photon Factory, KEK, Tsukuba, using fluorescence mode with a silicon drift detector (SDD). The polarization-dependent XAFS measurements were applied to two directions; (a) the horizontal direction of the sample in which the electric vector of X-ray, $\mathbf{E}$, is perpendicular to the *c*-axis of MgB₂ film where the *c*-axis is the perpendicular to the film plane; (b) the vertical direction in which $\mathbf{E}$ is inclined by 7 ° to the *c*-axis. The EXAFS analyses were performed by XANADU code [5] and FEFF 8.10 code [6]. We applied the non-linear least square fitting (curve fitting) method to EXAFS data and obtained the structural parameters. MgO powder sample was measured as a reference.

As preliminary measurements of superconductivity, T_c of the 30 nm MgB₂ films is 39 K, that of 20 nm is 20 K but no superconducting character was observed in the 10 nm film.

III. RESULTS AND DISCUSSION

Figure 1 shows the normalized X-ray absorption spectra for (a) the horizontal direction and (b) the vertical direction of 50 nm, 30 nm, 20 nm and 10 nm thick MgB₂ films deposited on ZnO and that for MgO powder.

Figure 2 shows the EXAFS function, $k\chi(k)$, for (a) the horizontal direction and (b) the vertical direction for 50 nm, 30 nm, 20 nm and 10 nm thick MgB₂ film on ZnO and MgO powder. $k\chi(k)$, for 20 nm film is close to that for MgO powder. There is a clear difference between thinner (10 and 20 nm) MgB₂ films and thicker (30 and 50 nm) films. The structure of 50 nm MgB₂ film is almost same as 150 nm film and shows hexagonal structure [3]. The result suggests that the local structure of the 10 nm

*This paper was presented at the conference "XAFS theory and nano particles", Chiba University, Chiba, Japan, July 18-20, 2012.

[†]Corresponding author: takaf@cc.hirosaki-u.ac.jp

TABLE I: The interatomic distance (r), the coordination number (N) and the root mean square displacement (σ) of the 30 nm and 50 nm MgB_2 films for the horizontal (H) and vertical (V) direction.

sample thickness	H/V	atomic type	r ($\text{\AA}$)	N	σ ($\text{\AA}$)
30 nm	H-1NN	Mg-B	2.48	10.0	0.14
30 nm	H-2NN	Mg-Mg	3.09	5.0	0.13
50 nm	H-1NN	Mg-B	2.55	12.0	0.13
50 nm	H-2NN	Mg-Mg	3.14	6.0	0.12
30 nm	V-1NN	Mg-B	2.48	9.8	0.17
30 nm	V-3NN	Mg-Mg	3.58	1.7	0.12
50 nm	V-1NN	Mg-B	2.55	12.0	0.17
50 nm	V-3NN	Mg-Mg	3.62	2.0	0.14

FIG. 1: Normalized X-ray absorption spectra for (a) the horizontal direction and (b) the vertical direction for 50 nm, 30 nm, 20 nm and 10 nm thick MgB_2 on ZnO. The result of MgO powder is included as a reference.

FIG. 2: EXAFS function, $k\chi(k)$, for spectra for (a) the horizontal direction and (b) the vertical direction for 50 nm, 30 nm, 20 nm and 10 nm thick MgB_2 on ZnO. The result of MgO powder is included as a reference.

and 20 nm thick sample was disturbed from the MgB_2 crystal.

Figure 3 shows the Fourier transforms (FTs) of $k\chi(k)$ for (a) the horizontal direction and (b) the vertical direction for 50 nm, 30 nm, 20 nm and 10 nm thick MgB_2 film on ZnO with MgO powder. Peaks around 2.0 $\text{\AA}$, 2.8 $\text{\AA}$ and 3.5 $\text{\AA}$ correspond to 1st nearest neighbor (1NN) Mg-B, 2NN Mg-Mg and 3NN Mg-Mg, respectively. FT for 30 nm MgB_2 film is similar to that for 50 nm. On the other hand, FT for 10 nm and 20 nm films have different structures from 30 nm and 50 nm films.

Above results indicate that the structure of 30 nm MgB_2 film is same as 50 nm and more thicker films and it can be understood that the superconducting performance

of 30 nm film is same as thicker ones. Now we applied the non-linear least square-fitting to k -space EXAFS data, in which the back-Fourier transform was performed with the window around 1-4 $\text{\AA}$, to obtain the structural parameters for 30 nm and 50 nm films more detail. We discuss only the 1st and 2nd nearest neighbor atomic pairs for horizontal direction and 1st and 3rd one for vertical in the present paper. The obtained structural parameters are summarized in Table I. In the fitting process of the polarization-dependent XAFS, the effective coordination number was taken into account but the net coordination number was appear in the Table I. The damping factor S_0^2 is determined from 50 nm film results. The local structure of 50 nm MgB_2 film is almost same as crystal one [3].

FIG. 3: Fourier transform of $k\chi(k)$ for (a) the horizontal direction and (b) the vertical direction for 50 nm, 30 nm, 20 nm and 10 nm thick MgB₂ on ZnO. The result of MgO powder is included as a reference.

On the other hand the interatomic distances (r) for 30 nm film are slightly shorter than that for 50 nm film. And the coordination number (N) is slightly smaller than that for 50 nm film. The root means square displacement (σ) for 30 nm film is larger than that for 50 nm. These results suggest that 30 nm MgB₂ film is deformed from the hexagonal MgB₂ structure in comparison to 50 nm and the thicker films.

Next we discuss the structure of 20 nm and 10 nm MgB₂ films. Figure 4 shows the XANES spectra of 20 nm and 10 nm as compared with that of MgO for (a) the horizontal direction and (b) the vertical direction. XANES of 50 nm film is also shown as a reference for hexagonal MgB₂. The 20 nm MgB₂ film shows closer XANES spectra to MgO. This suggests that 20 nm MgB₂ film contains a certain component of MgO phase. We tried to produce the XANES spectrum as the sum of that for 30 nm MgB₂ film and MgO powder. The mixed spectrum with 40% of MgO spectrum well reproduced the 20 nm spectrum for horizontal direction and that with 70% of MgO did for vertical direction. So about $55 \pm 15\%$ of MgO phase is included in the 20 nm MgB₂ film. These results suggest that the MgO phase exists between MgB₂ and ZnO substrate and the interfusion of MgO reduces T_c for 20 nm film.

On the other hand the XANES for 10 nm MgB₂ film is different from that for 20 nm films nor MgO powder. The characteristic structure can be observed around 1310-1320 eV. So we compared the XANES of 10 nm MgB₂ film with other typical Mg-O compounds. The structure

FIG. 4: XANES of 10 nm and 20 nm MgB₂ film for (a) the horizontal direction and (b) the vertical direction comparing to that of MgO. XANES of 50 nm film is also shown as a reference for hexagonal MgB₂.

of 10 nm film in the horizontal direction is similar to that of the diopside compound [7]. On the other hand, in the vertical direction the structure is close to spinel structure, $N=4$ [8]. As seen here, the 10 nm MgB₂ film has different structure from the hexagonal MgB₂ (50 nm film in Fig. 4), so it does not show any superconducting characters.

IV. CONCLUSIONS

We analyzed the local structure in 10 nm, 20 nm and 30 nm MgB₂ films deposited by MBE method on ZnO single crystal, using the polarization-dependent XAFS.

The structure of 30 nm MgB₂ film is similar to that for 50 nm one. This indicates that the quality of 30 nm MgB₂ film is high as 50 nm and thicker one. On the other hand, the structures of 10 nm and 20 nm MgB₂ films were different from 30 nm and 50 nm films. In 20 nm film, MgO phase exists in MgB₂/MgO interface. The 10 nm film show the different structure from 20 nm nor thicker than 30 nm films.

Acknowledgments

The authors would like to thank Dr. Y. Kitajima for their assistance with XAFS measurements. The synchrotron radiation experiments were performed at the Photon Factory in KEK under Proposal 2010G646.

-
- [1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitasni, and J. Akimitsu, *Nature* **410**, 63 (2001).
 - [2] Y. Harada, H. Yamaguchi, T. Takahashi, F. Izumida, H. Iriuda, T. Ohba, K. Meguro, M. Yoshizawa, and T. Kagaku, *J. Cryogenic Soc. Jpn.* **41**, 474 (2006).
 - [3] T. Miyanaga, T. Kanno, Y. Fujine, J. Araaki, and M. Yoshizawa, *J. Electron Spectrosc. Relat. Phenom.* **184**, 254 (2011).
 - [4] Y. Harada, T. Takahashi, H. Iriuda, M. Kuroha, Y. Nakanishi, and M. Yoshizawa, *Physica C* **426-431**, 1453 (2005).
 - [5] H. Sakane, T. Miyanaga, I. Watanabe, N. Matsubayashi, S. Ikeda, and Y. Yokoyama, *Jpn. J. Appl. Phys.* **32**, 4641 (1993).
 - [6] A. L. Ankudinov and J. J. Rehr, *Phys. Rev. B* **58**, 7565 (1998).
 - [7] Ph. Ildefonse *et al.*, *Nucl. Instrum. Methods Phys. Res. B* **97**, 172 (1995).
 - [8] J. A. van Bokhoven, J. C. A. A. Roelofs, K. P. de Jong, and D. C. Koningsberger, *Chem. Eur. J.* **7**, 1258 (2001).