

**Study of the Sputtered MgB<sub>2</sub> film on Al<sub>2</sub>O<sub>3</sub> by X-ray Absorption Spectroscopy**

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In our laboratory we successfully produced thin films on Al<sub>2</sub>O<sub>3</sub> by sputtering a target, which is made of a mixture of MgB<sub>2</sub> (commercial powder) and Mg, and went post-annealing process under different conditions. However, the films were not axial oriented and their superconductivity was not as great as MgB<sub>2</sub> powders. We study the B and Mg K-edge absorption spectra and find followings: 1. The sputtered film (before ex situ annealing treatment) contains small amount of B<sub>2</sub>O<sub>3</sub> due to residual oxygen in the vacuum chamber, and unknown Mg compound. No signal of MgO is observed. 2. Under annealing temperature at 900°C, B<sub>2</sub>O<sub>3</sub> is reduced to B by reacting with Mg and MgO is formed. No superconductivity was found. 3. Under annealing temperature at 600°~700°C, the  $T_c$  increases from 11.5 K to 25.5 K. The chemical shift of the pre-edge of the Mg K-absorption edge is greater as compared with that of MgB<sub>2</sub> powder ( $T_c = 39$  K). The Mg K-absorption spectrum indicates that the sample contains some amount of MgO.

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**I. INTRODUCTION**

The discovery of ~40 K superconductivity in MgB<sub>2</sub> [1] has led to a great deal of interest in exploring ways to make high-quality thin films [2–5], not only for understanding the mechanism of the superconductivity of this simple metallic compound, but also for industrial applications. Annealing boron films under a saturated magnesium vapor was found to be able to form MgB<sub>2</sub> films. In fact, Some *c*-axis oriented epitaxial films of MgB<sub>2</sub> were produced on Al<sub>2</sub>O<sub>3</sub>(1 $\bar{1}$ 02) substrate in using films of boron growing by laser deposition [6,7]. Yet, using films of boron growing by the method of thermal evaporation or magnetic ion sputtering was rarely reported. We have made films of boron by the latter two methods and went through the post-annealing process in niobium cells as well as copper cells at 900°C for various durations, from 30 min. to 15 hr., and no MgB<sub>2</sub> films were formed. However, we obtained a gold shining look film, a MgB<sub>2</sub> film with superconducting transition temperature at 25 K by post annealing a precursor film at lower temperature 700°C for 20 minutes. The precursor film was made on Al(1 $\bar{1}$ 02) by ion sputtering a target of magnesium-rich MgB<sub>2</sub>.

We felt that the physical structure of precursor films plays a significant role while forming good  $\text{MgB}_2$  films under the post-annealing process. We therefore, conduct the investigation of the precursor films and the films that went through the post-annealing process by measuring the x-ray absorption near-edge spectrum (XANES). Since the XANES of B K edge and Mg K edge can reveal not only the feature of the hole states in  $\text{MgB}_2$  [8–11] but also the contaminations, such as the oxidized boron or magnesium and other compounds, that may show up in the sample.

## II. EXPERIMENTAL DETAILS

### II-1. Sample preparation

A mixture of powders of  $\text{MgB}_2$  (Alfa Aesar, 99.9%) and Mg (Alfa Aesar, 99.8%) in a molar ratio of 1:1 or 1:2 was well mixed and ground and pressed under a static pressure of 22 MPa into a disk of 2.0 inches in diameter. The disk is then annealed at  $600^\circ\text{C}$  for 1 hr. in a furnace in flowing argon to form a target of Mg-rich  $\text{MgB}_2$  for ion sputtering. The sputtering chamber was evacuated to at least  $5.0 \times 10^{-6}$  torr and then filled with argon (99.99%) until the pressure is  $2.3 \times 10^{-3}$  torr. The operation power was 60 W and the substrate [a (1 $\bar{1}$ 02)  $\text{Al}_2\text{O}_3$ ] remained unheated. A silver-white film (a precursor film) was formed under ion sputtering for 2 hrs. The thickness of the film was measured by a Surface Texture Measuring System (Sloan Technology Corp.) to be about 600 nm.

A tantalum tube (with inner diameter of 5 mm and wall thickness of 0.08 mm), containing the as grown precursor film, together with 0.3 g magnesium turnings (CERAC, 99.9%) was put into a oxygen-free copper cell. The oxygen-free copper cell was designed to be airtight. The copper cell was then evacuated to  $5 \times 10^{-6}$  torr and sealed with an indium gasket and annealed in a furnace filled with one atmosphere of the mixing gas consisting of 95% of argon and 5% of hydrogen at a rapid rising temperature and finally quenched in liquid nitrogen. Various annealing temperature and annealing time were tried. We find that there is only a narrow window in which the  $\text{MgB}_2$  film can be formed. The temperature is limited to  $700^\circ\text{C}$  to  $600^\circ\text{C}$  and the annealing time is within 20 minutes. At  $600^\circ\text{C}$  we saw no change of the Mg turnings. This is quite reasonable for the melting point of magnesium metal being  $650^\circ\text{C}$  at one atmosphere. In the measurement of XRD, we did not observe any axial oriented peaks. In fact, we hardly observed the polycrystalline peaks, either. The strong peaks of the substrate could mar these peaks. Nevertheless, we observed the superconductivity of the films. In Table I, we list the annealing conditions for the films. Also listed are the onset superconducting transition temperature  $T_c$  and the width  $\Delta T_c$ , as measured by the four-point-probe method. The  $R$ - $T$  curves so obtained are shown in Fig. 1.

We used an atomic force microscope (AFM) to look into the microstructure of the films. Fig. 2 shows the typical pictures; (a) for the precursor film and (b) for the post annealed film. Both of them show the films are made of small clusters with fine particles in the size of about 5 nm. Apparently the film grows through a clustering process.

TABLE I: The conditions for which the films were made. The  $T_c$  is the onset superconducting transition temperature determined from  $R$ - $T$  curves. Also shown is the onset superconducting transition temperature of the commercial powders determined from the susceptibility versus temperature curves.

Films	Target for sputtering (Mg:B)	Annealing Temp./Time ( $^{\circ}\text{C}/\text{min.}$ )	$T_c(\rho=0)$ (K)	$\Delta T_c$ (K)
S1	2:1	750/20	—	—
S2	1:1	600/10	11.6	1
S3	1:1	700/20	21.3	1
S4	2:1	700/20	25.6	2
S5*	—	—	39.0	—

\* S5 is a sample made of commercial powders, the  $T_c$  is determined from the susceptibility measurement by using a SQUID

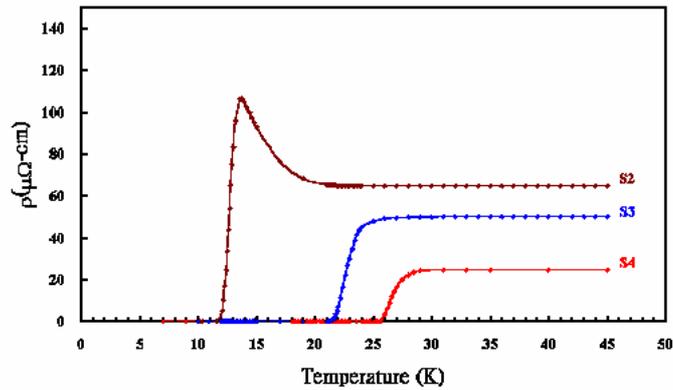


FIG. 1: The  $R$ - $T$  curves of the films of S2, S3, and S4.

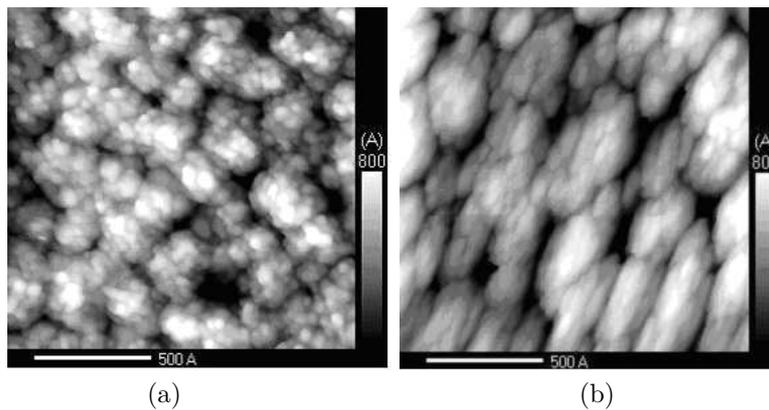


FIG. 2: A typical microstructure of (a) the precursor film and (b) the post annealed film, as measured by an AMF.

## II-2. X-ray absorption near-edge spectrum (XANES) measurements

The synchrotron radiation of a 1.5 GeV electron storage ring at the National Synchrotron Radiation Research Center (NSRRC), Taiwan, R.O.C., was monochromalized by a spherical-grating monochromator [12] for the measurement of the K-edge XANES of B, Mg and O (the reason for O K-edge measurement will be clear later). Gratings with 400  $l/mm$  and 200  $l/mm$  are used for the measurement of B K-edge XANES, while a grating with 1200  $l/mm$  is used for the measurement of Mg and O K-edge XANES. The openings of the entrance and exit slits are kept to 30  $\mu m$ . Total fluorescence yields of boron and magnesium were recorded with either a micro-channel plate (MCP) or a seven-element Ge detector. However, we used only MCP to measure the B K-edge XANES for two reasons; one is that the efficiency of the seven-element Ge detector is very low at 190 eV, and the other is that the beams contain third order harmonics even the grating with 200  $l/mm$  is used. Since the energy of O K-edge (530 eV) is about three times higher than that of B K-edge (188 eV), the high-rising tail of any oxide signal can bury the signal of B K-edge XANES for a low efficiency detector, especially when the thin film contains oxide impurities or the thickness of the film is not thick enough to block the signals resulting from the  $Al_2O_3$  substrate. Using the soft x-ray mass absorption coefficients that is derived on the basis of the x-ray attenuation cross sections for elements [13], we estimate the mean free path of the photons at 190 eV in  $MgB_2$  is about 600 nm. Yet, we still saw the influence of the background resulting from the substrate, even a MCP was used for the measurement of the x-ray fluorescence. It appears that our films are not thick enough to block the signals resulting from the substrate.

In energy calibrations of the absorption spectra, we refer to the energy of the pre-edge of CuO as 530.1eV (the third harmonics of 176.7eV) [14] and the threshold of the Mg K-edge of the Mg metal as 1303.0 eV [15]. All spectra has been normalized to the intensity of the photo beams, which was measured by a nickel mesh putting in front of the sample chamber. In the process of x-ray fluorescence measurements, we also recorded the sample current that is sensitive to the surface effect of the film.

## III. RESULTS AND DISCUSSION

### III-1. The K-edge XANES of boron and magnesium in the precursor film

In the left column of Fig. 3, we show the K-edge XANES of boron for (a) the precursor film, (b) the thermal evaporated film of boron, and (c) the powder of  $B_2O_3$ . These spectra indicate clearly the precursor film contains both boron and boron oxide ( $B_2O_3$ ). The thermal evaporated film of boron is not oxidized. The right column of Fig. 3 shows the Mg K-edge XANES for (e) the precursor film, (f) magnesium metal powders, and (g)  $MgB_2$  powders. It appears that there is a positive chemical shift of the Mg K-edge of the precursor film with respect to that of magnesium metal but no sign of the existence of MgO (its K-edge XANES is shown in Fig. 5). In combination of information in all these spectral data, we conclude that the precursor film contains boron, boron oxide, and magnesium compounds whose chemical shift of Mg K edge is close to that of MgO. No sign of pure magnesium

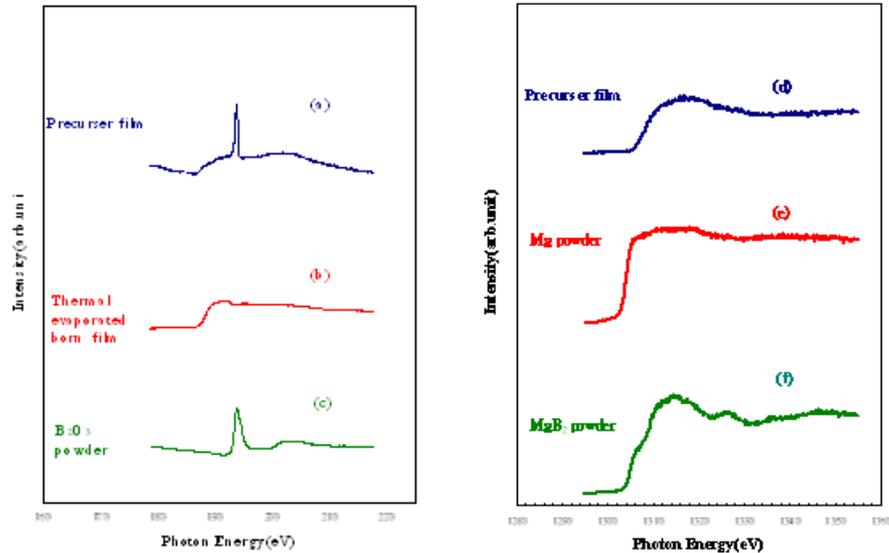


FIG. 3: The B K-edge XANES for (a) the precursor film, (b) the thermal evaporated boron film, (c) powders of  $\text{B}_2\text{O}_3$ , and the Mg K-edge XANES for (d) the precursor film, (e) powders of Mg metal, (f) powders of  $\text{MgB}_2$ .

metal appears.

### III-2. The B K-edge XANES of the $\text{MgB}_2$ films

Fig. 4 shows the B K-edge XANES for sample listed in Table 1 and the  $\text{MgB}_2$  powder (99.8%, Alfa Aesar). For clarity, a linear background, as extrapolated from the spectral region between 175 eV and 180 eV, was subtracted for those spectra (except that of  $\text{MgB}_2$  powders). This background presumably results from oxygen X-ray absorption around the energy of its K edge because of the existence of the third harmonics in the photo beams. The X-ray absorption spectra that were taken both in the beam energy region of B K-edge and O K-edge for the  $\text{Al}_2\text{O}_3$  substrate (not shown) appeared identical, indicating the existence of the third order of harmonics in the beams.

There are three distinguishable peaks appearing in Fig. 4 for  $\text{MgB}_2$  powders (sample S5); peak A corresponds to the transitions to the hole states at the Fermi level [8, 9, 10], peak B results from a strong resonance in the elastic scattering [9], and peak C is associate with boron oxides [9].

For films, most of them have peak B and peak C, and it appears that the intensity of the peak C decreases as  $T_c$  increases. This suggests that the existence of  $\text{B}_2\text{O}_3$  in the film dismantles the superconductivity of the film. Presumably  $\text{B}_2\text{O}_3$  is the leftover of the precursor film after annealing. We shall show that most of  $\text{B}_2\text{O}_3$  reacts with Mg

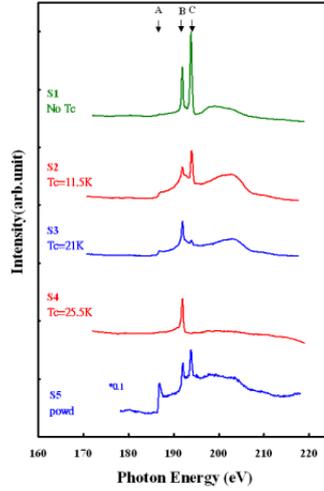


FIG. 4: The B K-edge XANES of the  $\text{MgB}_2$  films (S1 - S4) studied in this work. The B K-edge XANES of commercial powders (S5) is also shown.

and becomes  $\text{MgO}$  and  $\text{MgB}_2$  at the annealing temperature  $700^\circ\text{C}$ . At lower annealing temperature, this chemical reaction is not completed and thus has  $\text{B}_2\text{O}_3$  remained. This statement is in accordance with the fact that the spectral intensity of peak C decreases with the annealing temperature (Table I). As to the other two peaks the peak A and peak C, no consistent change in their intensities with their superconductivities are observed. However, we are surprised that the peak A is hardly observed for the sample S4, which has the highest  $T_c$  among the films we made. It suggests that the number of hole states at the Fermi level with boron  $2p$  character is not significant to the superconductivity of  $\text{MgB}_2$ , at least up to  $T_c = 25$  K.

### III-3. The Mg K-edge XANES of the $\text{MgB}_2$ films

All the Mg K-edge XANES of  $\text{MgB}_2$  films are normalized to the same in the energy range far from the edge, which presumably contains only the continuous states of magnesium. Some typical normalized spectra are shown in Fig. 5. Included also the Mg K-edge XANES of powders of  $\text{MgB}_2$ , Mg metal and  $\text{MgO}$  for comparisons. One notes that there are near-edge structures for all compounds; notably three peaks A, B, and C for  $\text{MgO}$  and a "pre-edge" peak P for  $\text{MgB}_2$  powders and  $\text{MgB}_2$  films, a characteristic peak for the superconducting  $\text{MgB}_2$ . The energy of the pre-edge peak becomes higher for  $\text{MgB}_2$  films than that for  $\text{MgB}_2$  powders, indicating that the energy of this peak is relevant to the superconductivity. The shift of the energy of the pre-edge in the films can also become visible after using two Gaussian curves to deconvolute the structures of the edge. The light curves in Fig. 5 are the Gaussian curves, and the heavy curve is their sum. The pre-edge energy shifts are respectively, 1.1 eV and 1.8 eV for the pre-edges of the sample S4 ( $T_c \sim 25$  K) and the sample S2 ( $T_c \sim 11.5$  K) with respect to that of the  $\text{MgB}_2$  powder (S5,  $T_c \sim 39$  K).

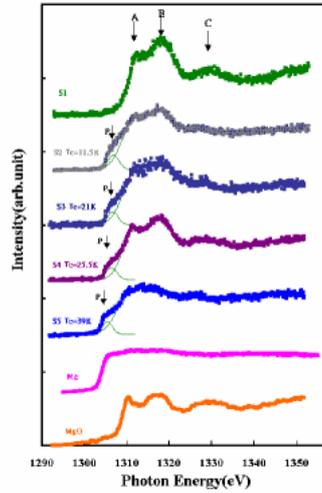


FIG. 5: Same as Fig. 4, but for Mg K-edge XANES.

The pre-edge peak can be interpreted as the transition from the  $1s$  states to the  $2p$  states. A theoretical calculation indicates that there are density of states of the local Mg  $p$  band near the Fermi level, which is empty [16].

The existence of peak A, B, and C in the spectra of the films suggest that these films contains a certain amount of MgO, which as aforementioned, results from the reaction of the  $\text{B}_2\text{O}_3$  with Mg in the annealing process. This fact can be demonstrated by comparing the Mg K-edge XANES of the precursor film in Fig. 3, and that of the post annealed films ( $\text{MgB}_2$  film) in Fig. 5. There are essentially no near-edge structures appearing in the spectrum of the precursor film, very different from the spectrum of the  $\text{MgB}_2$  films. The film of S1 that is not superconducting down to about 5 K having similar spectral feature to that of MgO, and therefore, it contains substantially amount of MgO. The amount of MgO in  $\text{MgB}_2$  film will affect the superconductivity of the film, more for poorer superconductivity.

One notices that the chemical shift of MgO with respect to Mg metal is the greatest among all samples we investigated. It results apparently from the ionic character of MgO. In this sense, the ionicity of  $\text{MgB}_2$  powder is not as great as MgO, since the energy of its edge (excludes the pre-edge peak) is about 3.0 eV from the edge of the Mg metal, in contract to 5.0 eV for the edge of MgO. It is in accordance with the theoretical calculation that indicates there is an electron transfer between the boron plane and the magnesium plane [17]. The ionicity of  $\text{MgB}_2$  is thus less than that of MgO.

#### IV. CONCLUSION

In this work we report the results of the X-ray absorption spectroscopic study of the precursor films and the post annealed films of  $\text{MgB}_2$  around the K-edge of boron and magnesium. The precursor films were made on  $\text{Al}_2\text{O}_3(1\bar{1}02)$  substrates by ion sputtering a

target of Mg-rich  $\text{MgB}_2$ . We observed that the precursor film contains certain amount of  $\text{B}_2\text{O}_3$  and unknown magnesium compound. The existence of  $\text{B}_2\text{O}_3$  in the precursor film can be the reason for the deterioration of the quality of the  $\text{MgB}_2$  film since  $\text{MgB}_2$  is produced partly by the reaction of  $\text{B}_2\text{O}_3$  with Mg in the post annealing process, and MgO is the byproduct in the reaction. The existence of MgO in the film is suggested to dismantle the superconductivity of the film. The degree of covalent bonding between Mg and B appears to affect the superconductivity of the film.

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