Observation of superconductivity in thick amorphous Mg_xB_{1-x} films

S. Okuma, S. Togo, and K. Amemori
Research Center for Low Temperature Physics, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-8551, Japan
(Received 23 October 2002; published 23 May 2003)

We report the observation of superconductivity in homogeneously disordered thick films of amorphous Mg_xB_{1-x} with $x=0.29-0.39$. We find that the superconducting-transition temperature T_c changes smoothly as a function of x, exhibiting a peak ($T_c \approx 6.1$ K) at $x \approx 0.33$ ($\equiv x_p$). Seven films studied in this work are classified into two groups. For films with $x<x_p$ the slope of the critical field $B_0(T)$ where the dc resistivity vanishes is larger than that for films with $x \geqslant x_p$, indicating that there is a difference in the electronic and/or vortex states between the two groups.

DOI: 10.1103/PhysRevB.67.172508 PACS number(s): 74.25.Fy, 74.25.Ha, 74.62.−c

Since the discovery of superconductivity in MgB_2 at about 39 K,[1] much effort has been devoted to fabricating high-quality crystals. To date, films with a highly *c*-axis-oriented crystal structure,[2–7] as well as bulk single crystals,[8–14] have been fabricated. These samples are considered to be sufficiently clean, having the low resistivity in the normal state at 40 K ($\rho_n \sim 0.1-10\ \mu\Omega$ cm). However, the superconducting properties, as well as the values of ρ_n, are dependent on preparation methods. The superconducting-transition temperature T_c for the crystal samples stays close to 39 K, while somewhat lower values of T_c ($\sim 22-39$ K) have been reported for the film samples.[15,16] The upper critical field $B_{c2}(0)$ in the limit of zero temperature ($T \rightarrow 0$) ranges from ~ 4 T for single crystals, where the field is applied perpendicular to the Mg and B planes, to 15 T for wires and polycrystallines. On the basis of data of dc resistivity and magnetic measurements, the possible vortex phase diagram in the field-temperature (B-T) plane has been actively discussed. One of the most striking features is the extremely broad ''vortex-liquid phase'' which grows progressively with decreasing temperature.

Compared with clean samples, very little has been studied about the dirty samples.[16–18] It is interesting to study amorphous (*a*-)Mg_xB_{1-x} films where disorder is microscopic and extremely strong. Of course it is not evident whether we can fabricate *a*-Mg_xB_{1-x} films, and even if we can fabricate them, it is not clear whether they exhibit superconductivity. To date, several amorphous alloy films are known to exhibit superconductivity.[19–22] For instance, in molybdenum-base *a*-Mo_xGe_{1-x} (Ref. 20) and *a*-Mo_xSi_{1-x} films, T_c is varied as a function of x. Mo is itself a superconductor with a bulk T_c of 0.9 K, while T_c's of these amorphous alloy films are much higher than 1 K for moderate Mo concentration x: e.g., T_c of the 100-nm-thick *a*-Mo_xSi_{1-x} films reaches 7 K for $x=0.7$.[19]

In this paper we report the observation of superconductivity in thick *a*-Mg_xB_{1-x} films with varying x. The *a*-MgB_2 films which exhibit superconductivity have been already reported by Kúš *et al.*[16] However, the preparation method and superconducting properties are very different from those in the present study, suggesting that the microscopic or mesoscopic structure of the films is also different. The films reported on in Ref. 16 were deposited on flexible plastic substrates and subsequently heated to approximately 600 °C. The onset temperature of the superconducting transition was about 29 K, which is much higher than the T_c values of our films. We find that the superconducting properties, T_c and B_{c2}, for our films are similar to those for conventional amorphous alloy films, such as thick (100 nm) *a*-Mo_xSi_{1-x} films.[23,24] The T_c changes systematically and smoothly as a function of x, exhibiting a peak ($T_c \approx 6.1$ K) at $x \approx 0.33$ ($\equiv x_p$). Seven films studied in this work are classified into two groups. For films with $x<x_p$ the slope of the critical field $B_0(T)$ where the dc resistivity vanishes is larger than that for films with $x \geqslant x_p$. The ''vortex-liquid phase'' is even narrower than that reported for clean MgB_2 samples but somewhat broader than that for thick *a*-Mo_xSi_{1-x} films.[23,24] The preliminary results, the preparation method, and characterization of the *a*-Mg_xB_{1-x} films are presented elsewhere.[25]

The films were prepared by coevaporation of pure Mg (99.9 %) and B (99.9 %) from electron-beam crucibles onto a glass substrate held at room temperature. The vacuum was $\sim 10^{-10}$ Torr before deposition and approximately 10^{-8} Torr during deposition. In order to obtain a series of samples with continuously changing x for fixed thickness, we employed a gradient deposition technique.[22,26] The edges of the film were trimmed by a sharp stylus to avoid ambiguity in thickness. The shape of the film was not perfectly rectangular and hence, there is some ambiguity in determining ρ_n. The size of our film was 2.5 mm in length, 0.5–1 mm in width, and 290 nm in thickness. The gradient of Mg concentration, which was in parallel to the direction of the sample width, was smaller than 0.09%/mm, which corresponds to the T_c variation of 0.02 K (films 4–6)-0.13 K (film 1) within each film. We prepared seven films with x ranging from 0.39 (film 1) to 0.29 (film 7). The absolute values of x were not determined directly from the experiments but merely calculated from the deposition rate. The electrical resistivity ρ was measured by the conventional four-terminal ac locking and dc methods. The magnetic field was directed perpendicular to the plane of the film.

We have taken a transmission-electron micrograph (TEM) and an electron-diffraction pattern of the 10-nm-thick Mg_xB_{1-x} films with $x=0.4$ and 0.3. In either film we do not observe any sign of granular structure down to about 1 nm. Typically shown in Fig. 1 is the TEM image of the 10-nm-

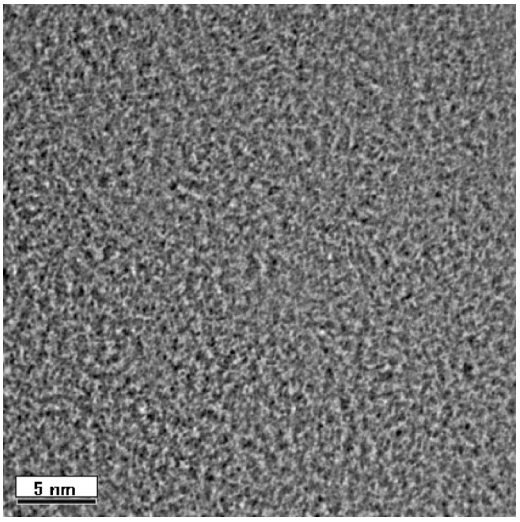

FIG. 1. The 33 nm×33 nm TEM image of the 10-nm-thick Mg_xB_{1-x} film with $x=0.3$ deposited on a thin a-C film.

thick Mg_xB_{1-x} film with $x=0.3$ deposited on a thin a-C film at room temperature. The very small structure (<1 nm) that is visible in Fig. 1 is most likely attributed to that of a-C. We thus consider that a-Mg_xB_{1-x} films can be fabricated at room temperature by coevaporation of Mg and B at least within the x range studied.[27]

The normal-state resistivity ρ_n at 10 K shows a trend to increase as x decreases, $\rho_n \sim 4\times10^2$ $\mu\Omega$ cm for film 1 ($x=0.39$) and 7.4×10^2 $\mu\Omega$ cm for film 7 ($x=0.29$), as is similar to the case with a-Mo_xSi_{1-x} films.[22] We notice, however, that ρ_n for films 1–4 stays almost constant within our experimental resolutions. The reason is not clear, but it may be partly attributed to ambiguity in determining ρ_n mentioned above. As is shown below, T_c, which is not dependent on the sample size, exhibits a systematic change against x, indicating that electronic states for films 1–7 indeed change as a function of x.

Typically shown in Fig. 2 is the temperature dependence of the resistivity $\rho(T)$ for film 3 in different magnetic fields. Upon cooling from room temperature, $\rho(T)$ in $B=0$ stays

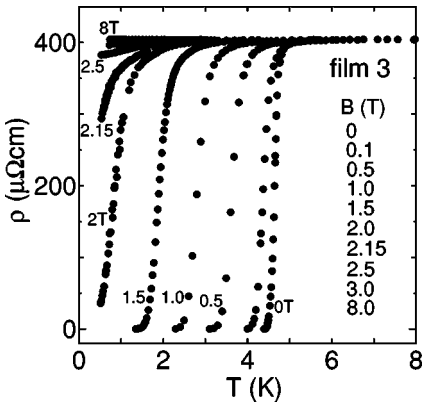

FIG. 2. Temperature dependence of the resistivity $\rho(T)$ for film 3 with $x=0.36$ in various magnetic fields B, which are listed in the figure (from right to left).

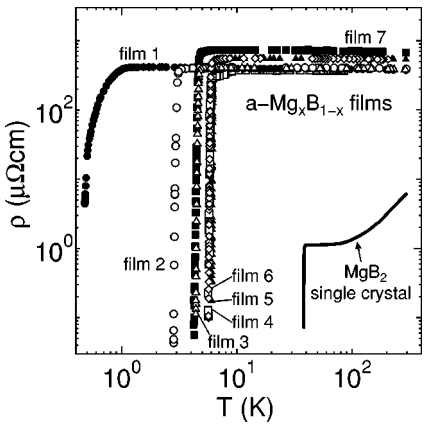

FIG. 3. Temperature dependence of the resistivity $\rho(T)$ in zero field for films 1–7 with $x=0.39$–0.29 and for the single-crystal MgB_2 sample from the data in Ref. 9.

almost constant or increases very slowly without showing any sign of superconductivity at $T\sim39$ K. With further decreasing T, $\rho(T)$ exhibits a sudden decrease at around 5 K and falls to zero at 4.4 K. The superconducting-transition (zero-resistivity) temperature $T_c=4.4$ K is much lower than $T_c=39$ K for MgB_2 crystals. Here, we define the onset temperature T_{on} as a temperature at which ρ decreases to 90% of ρ_n (10 K). The width of the transition curve, as defined as $\Delta T=T_{on}-T_c$, is 0.34 K. In $B=0.1$ T, the transition width ΔT is larger than that in zero field. With further increasing $B(>0.1$ T), $\Delta T(B)$ stays almost unchanged or increases very slowly. Similar behavior is observed for the rest of the films.

Figure 3 illustrates the temperature dependence of the resistivity $\rho(T)$ in zero field for films 1–7. Also shown is $\rho(T)$ in $B=0$ for the single-crystal MgB_2 sample from the data of Ref. 9. The normal-state resistivity ρ_n for our a-Mg_xB_{1-x} films lies in the range 10^2–10^3 $\mu\Omega$ cm, which is of the same order of magnitude as ρ_n for thick (100 nm) a-Mo_xSi_{1-x} films,[23] but much larger than 1–10 $\mu\Omega$ cm for the single-crystal MgB_2.[9] The transition temperature T_c (T_{on}) for the a-Mg_xB_{1-x} films is dependent on x. In Fig. 4 we plot T_c for seven films as a function of boron concentration $1-x$. We can see that T_c changes systematically and smoothly against

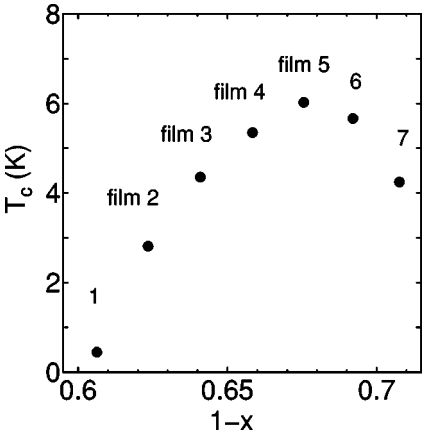

FIG. 4. T_c for films 1–7 plotted against $1-x$.

x, showing a peak at $1-x_p \approx 0.675 \pm 0.005$ ($x_p \approx 0.325 \pm 0.005$) for film 5. The maximum value of $T_c = 6.1$ K is close to that ($T_c \sim 7$ K) for thick a-Mo_xSi_{1-x} films. It is interesting to note that x_p corresponds to 1/3 (i.e., MgB_2). We cannot tell definitely, however, whether x_p exactly coincides with 1/3, since the absolute value of x cannot be determined precisely from the present experiment.

One may question that the variation in T_c observed among films 1–7 may imply the occurrence of superconductivity in different stoichiometric phases of the Mg-B system, such as MgB_4 ($x=0.20$) and MgB_6 ($x=0.14$) or other unknown Mg_xB_{1-x} compounds.[15] However, the following facts suggest that such a possibility is weak: (i) The range of x (=0.29–0.39) studied in this work is narrow, (ii) the resistive transition $\rho(T)$ is smooth and relatively sharp except for film 1, and (iii) the variation of T_c with x is smooth, which would not be expected if our film was composed of more than two phases with different T_c. The shape of the transition curve $\rho(T)$ for film 1 looks broader, though smooth, as compared to $\rho(T)$ for the rest of six films 2–7. We consider that part of the reason is due to T_c variation within the sample resulting from a gradient of x, since dT_c/dx is largest for film 1 (Fig. 4). The results obtained here are different from what has been reported for polycrystalline $Mg_{1-x}B_2$ samples with $0 \leqslant x \leqslant 0.15$ in which percolative superconductivity is observed.[18]

Let us consider the possible phase diagram in the mixed state. We present the characteristic fields vs T for the selected films 2, 3, and 5 [Fig. 5(a)] and films 6 and 7 [Fig. 5(b)] extracted from the $\rho(T)$ data in various B on the basis of different criteria: onset $B_{0.9}$ (open symbols) and completion B_0 (full symbols). Here, $B_{0.9}$ and B_0, respectively, represent the points where ρ decreases to 90% and 0.01% of ρ_n (10 K). In the vortex phase diagram in the B-T plane, $B_{0.9}$ and B_0 are roughly identified with the upper critical field B_{c2} and the ''melting field'' (the first-order or second-order transition), respectively. The whole shapes of $B_{c2}(T)$ [or $B_0(T)$] for films 1–5 are similar to each other, while the slope of the $B_{c2}(T)$ [or $B_0(T)$] lines for films 6 and 7 is remarkably larger than that for films 1–5. This is clearly seen by comparing, for example, $B_{c2}(0)=2.4$ T for film 3 with $B_{c2}(0)=5.4$ T for film 7, whose $T_c=4.3$–4.4 K is nearly identical to each other.

In Fig. 6 we plot $B_0(0)$ for films 2–7 against T_c, where $B_0(0)$ is obtained by extrapolating $B_0(T)$ to $T=0$. For film 1, $B_{c2}(0)$ is plotted instead of $B_0(0)$, since $B_0(0)$ is not determined unambiguously within the T range measured. All the films studied in this work are classified into two groups; films 1–5 with $x \geqslant x_p$ and films 6 and 7 with $x < x_p$. In either group $B_0(0)$ roughly follows the linear relation, $B_0(0)=aT_c$, where $a=0.47$ and 0.80 T/K for films with $x \geqslant x_p$ and $x < x_p$, respectively. More precisely, film 5 may be located in the intermediate regime between two groups. The results presented here indicate that there is a difference in the electronic and/or vortex states between the two groups. The superconducting properties for films 6 and 7 with $x < x_p$ are most likely dominated by localization effects caused by reduction of carrier concentration x.[22,26,28] Although the physical mechanism responsible for superconductivity in a-Mg_xB_{1-x} films is still unknown, we hope the present results will provide some useful information in preparing high-quality MgB_2 films and in understanding the mechanism of superconductivity in amorphous alloy films.

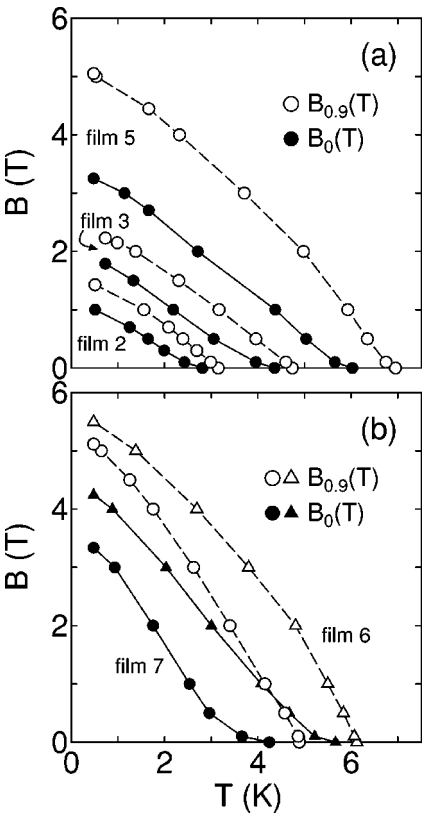

FIG. 5. Characteristic fields vs T for (a) films 2, 3, and 5 and (b) films 6 and 7: onset $B_{0.9}$ (open symbols) and vanishing resistivity B_0 (full symbols). Here $B_{0.9}$ and B_0, respectively, represent the points where ρ decreases to 90% and 0.01% of ρ_n (10 K). The dashed and full lines are guides to the eye.

As pointed out earlier, there is big difference between the values of T_c ($\leqslant 6.1$ K) obtained in the present work for

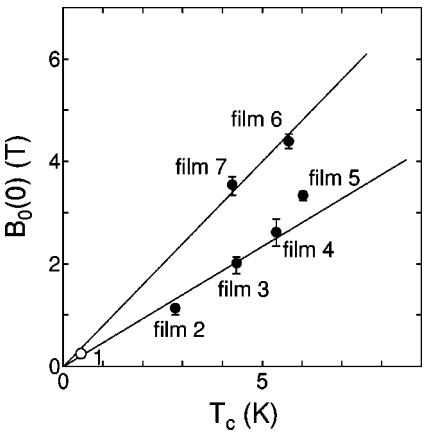

FIG. 6. $B_0(0)$ (filled circles) for films 2–7 plotted against T_c. For film 1, $B_{c2}(0)$ (open circle) is plotted instead of $B_0(0)$. The straight lines represent linear fits.

a-Mg_xB_{1-x} films and the value of $T_c \approx 29$ K reported in Ref. 16 for a-MgB_2 films. The higher T_c reported in a-MgB_2 films, together with the fact that the bulk of the a-MgB_2 films exhibits a fully stoichiometric composition of Mg and B, may be due to postannealing at temperatures higher than 600 °C.[16] We assume that the annealing process may lead to formation of crystallinelike grains with higher T_c ($\gg 6$ K), which may not be detected experimentally. Actually, it has been reported by Kúš and co-workers that the superconducting properties depend strongly on the conditions of annealing and that the granular nature has been suggested by the critical current density.[16]

Finally, we comment on the ''vortex-liquid phase.'' We have commonly observed that the $B_{c2}(T)$ line in the B-T phase diagram runs nearly parallel to the $B_0(T)$ line except near T_c down to the lowest T measured. The similar feature is observed for thick a-Mo_xSi_{1-x} films with various x.[23,24,28] The behavior observed for a-Mg_xB_{1-x} and a-Mo_xSi_{1-x} films is markedly different from what has been reported for MgB_2 single crystals and dense polycrystalline wires, where the width of the vortex-liquid phase $\Delta B(T)$, as defined as $\Delta B(T) = B_{c2}(T) - B_0(T)$, grows remarkably upon cooling.

To summarize, we report the observation of superconductivity in a-Mg_xB_{1-x} films with $x = 0.29 - 0.39$. We find that T_c changes smoothly as a function of x, exhibiting a peak ($T_c \approx 6.1$ K) at $x_p \approx 0.33$. Seven films studied in this work are classified into two groups. For films with $x < x_p$ the slope of the $B_0(T)$ line is larger than that for films with $x \geqslant x_p$, indicating that there is a difference in the electronic and/or vortex states between the two groups. The preliminary measurements of the ac complex resistivity[23,29] for the present a-Mg_xB_{1-x} films suggest the existence of the vortex-glass transition[30] at around B_0.

We thank A. Genseki and M. Morita for technical assistance. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture.

[1] J. Nagamatsu *et al.*, Nature (London) **410**, 63 (2001).
[2] H. H. Wen *et al.*, Phys. Rev. B **64**, 134505 (2001).
[3] W. Jo *et al.*, Appl. Phys. Lett. **80**, 3563 (2002).
[4] W. N. Kang *et al.*, Phys. Rev. B **65**, 134508 (2002).
[5] Hyeong-Jim Kim *et al.*, Phys. Rev. Lett. **87**, 087002 (2001).
[6] Z. W. Zhao *et al.*, Phys. Rev. B **65**, 064512 (2002).
[7] S. K. Gupta *et al.*, Phys. Rev. B **66**, 104525 (2002).
[8] S. Lee *et al.*, J. Phys. Soc. Jpn. **70**, 2255 (2001).
[9] Yu. Eltsev *et al.*, Phys. Rev. B **65**, 140501 (2001).
[10] A. K. Pradhan *et al.*, Phys. Rev. B **64**, 212509 (2001).
[11] Kijoon H. P. Kim *et al.*, Phys. Rev. B **65**, 100510 (2002).
[12] F. Manzano *et al.*, Phys. Rev. Lett. **88**, 047002 (2002).
[13] M. Zehetmayer *et al.*, Phys. Rev. B **66**, 052505 (2002).
[14] Y. Machida, S. Sasaki, H. Fujii, M. Furuyama, I. Kakeya, and K. Kadowaki, Phys. Rev. B **67**, 094507 (2003).
[15] S. R. Shinde *et al.*, Appl. Phys. Lett. **79**, 227 (2001).
[16] Peter Kúš *et al.*, Appl. Phys. Lett. **81**, 2199 (2002).
[17] S. R. Shinde, S. B. Ogale, A. Biswas, R. L. Greene, and T. Venkatesan, cond-mat/0110541 (unpublished).
[18] P. A. Sharma *et al.*, Phys. Rev. Lett. **89**, 167003 (2002).
[19] W. L. Johnson, C. C. Tsuei, S. I. Raider, and R. B. Laibowitz, J. Appl. Phys. **50**, 4240 (1979).
[20] J. M. Graybeal and M. R. Beasley, Phys. Rev. B **29**, 4167 (1984).
[21] N. Nishida *et al.*, Solid-State Electron. **28**, 81 (1985).
[22] S. Okuma, T. Terashima, and N. Kokubo, Solid State Commun. **106**, 529 (1998); Phys. Rev. B **58**, 2816 (1998).
[23] S. Okuma, Y. Imamoto, and M. Morita, Phys. Rev. Lett. **86**, 3136 (2001).
[24] S. Okuma, M. Morita, and Y. Imamoto, Phys. Rev. B **66**, 104506 (2002).
[25] S. Okuma, S. Togo, D. Sanno, K. Amemori, and M. Morita, in *Proceedings of the 2002 International Conference on Physics and Chemistry of Molecular and Oxide Superconductors, 2002, Hsinchu*, edited by C. C. Chi and M. K. Wu (Kluwer Academic/Plenum, Belgium, 2003) [J. Low Temp. Phys. **131**, 1111 (2003)].
[26] S. Okuma, S. Shinozaki, and M. Morita, Phys. Rev. B **63**, 054523 (2001).
[27] We do not definitely rule out the possibility of the presence of microcrystals in the 290-nm-thick films studied in this work, since we cannot perform TEM observation for the thick films due to a technical reason (Ref. 25).
[28] S. Okuma, S. Togo, Y. Imamoto, and F. Saito, Physica C **378-381**, 453 (2002); S. Okuma, S. Togo, and M. Morita (unpublished).
[29] S. Okuma and N. Kokubo, Phys. Rev. B **56**, 14 138 (1997); S. Okuma and M. Arai, J. Phys. Soc. Jpn. **69**, 2747 (2000).
[30] D. S. Fisher, M. P. A. Fisher, and D. A. Huse, Phys. Rev. B **43**, 130 (1991).