Epitaxial Growth of FeSe$_{0.5}$Te$_{0.5}$ Thin Films on CaF$_2$ Substrates with High Critical Current Density

Ichihiro Tsukada$^{1,5}$, Masafumi Hanawa$^{1,5}$, Takenori Akiike$^{2,5}$, Fuyuki Nabeshima$^{2,5}$, Yoshinori Imai$^{2,5}$, Ataru Ichinose$^{1,5}$, Seiki Komiyama$^{1,5}$, Tatsuo Hikage$^{3,5}$, Takahiko Kagawuchi$^{4,5}$, Hiroshi Ikuta$^{4,5}$, and Atsutaka Maeda$^{2,5}$

$^1$Central Research Institute of Electric Power Industry, Yokosuka, Kanagawa 240-0196, Japan
$^2$Department of Basic Science, The University of Tokyo, Meguro, Tokyo 153-8902, Japan
$^3$High Intensity X-ray Diffraction Laboratory, Nagoya University, Nagoya 464-8603, Japan
$^4$Department of Crystaline Materials Science, Nagoya University, Nagoya 464-8603, Japan
$^5$JST, TRIP, Chiyoda, Tokyo 102-0075, Japan

Received March 29, 2011; accepted April 18, 2011; published online May 9, 2011

In-situ epitaxial growth of FeSe$_{0.5}$Te$_{0.5}$ thin films is demonstrated on a nonoxide substrate CaF$_2$. Structural analysis reveals that compressive stress is moderately added to 36-nm-thick FeSe$_{0.5}$Te$_{0.5}$, which pushes up the critical temperature to above 15 K, showing higher values than that of bulk crystals. The critical current density at $T = 4.5$ K reaches $5.9 \times 10^4$ A cm$^{-2}$ at $\mu_0 H = 10$ T, and $4.2 \times 10^4$ A cm$^{-2}$ at $\mu_0 H = 14$ T. These results indicate that fluoride substrates have high potential for the growth of iron-based superconductors in comparison with popular oxide substrates.

$^*$E-mail address: ichiro@criepi.denken.or.jp

Since the discovery of iron-based superconductors,$^{1}$ much effort has been devoted to establish a thin-film growth technique of these compounds.$^{2-8}$ At an early stage, iron-chalcogenide superconductors$^{9}$ had been considered rather inappropriate for practical applications simply because of their low critical temperature ($T_c$). However, pressure-effect studies demonstrate that the potential $T_c$ of iron-chalcogenide superconductors is as high as 37 K,$^{10,11}$ which motivated us to begin the study of thin-film growth of FeSe$_{1-x}$Te$_x$. Through many reports,$^{12-16}$ one problem has gradually emerged; There is a close correlation between $T_c$ and the structure of the films grown epitaxially, but their lattice parameters are influenced by too many growth parameters, and the lattice parameters of the substrate material are not a dominant factor.$^{17-19}$ In other words, FeSe$_{1-x}$Te$_x$ can be grown epitaxially on a single-crystalline substrate, but the lattice parameters cannot be designed in accordance with those of the substrates. One of the possible reasons that we have previously proposed for this is oxygen contamination from oxide substrates,$^{18,19}$ and we actually confirmed the presence of oxygen at the interface of FeSe$_{1-x}$Te$_x$ grown on yttria-stabilized zirconia (YSZ) and LaSrAlO$_3$. In order to avoid this problem and further improve superconducting properties, it is important to investigate the film growth on nonoxide substrates. In this letter, we demonstrate an epitaxial growth on nonoxide single-crystalline substrates, CaF$_2$ ($a_0 = 5.463$ Å). Our results indicate that films with high-$T_c$ and high-J$_c$ can be obtained reproducibly on CaF$_2$ (100) substrates even with a thickness as small as approximately 40 nm. Several films showed a $T_c$ higher than that of bulk single crystals, strongly suggesting that the epitaxial strain effect moderately works on CaF$_2$(100).

All the films were grown by pulsed laser deposition from an FeSe$_{0.5}$Te$_{0.5}$ target, as was described elsewhere.$^{16,18,19}$ Substrate temperature, laser repetition rate, and back pressure are 280°C, 10 Hz, and $\sim 10^{-5}$ Torr, respectively. Commercially available CaF$_2$(100) substrates were used for the present experiments. A specially designed metal mask was put directly on the substrate to make the films into a six-terminal shape, in which the dimensions of the measured area are 0.95 mm length and 0.2 mm width. We prepared four very thin films with thicknesses of approximately 40 nm named C1 (36 nm), C2 (38 nm), C3 (40 nm), and C4 (42 nm), and two relatively thick films with thicknesses of approximately 150 nm named C5 (150 nm) and C6 (175 nm). The resistivity and critical current were measured using a physical property measurement system (PPMS) under magnetic fields of up to 14 T.

All the films are c-axis oriented as shown in Fig. 1(a), and no reflections originating from an impurity phase are detected. In-plane orientation is confirmed for C1, C3, and C5 by a four-circle diffractometer. Figure 1(b) shows the ϕ scans of the 101 reflection of FeSe$_{0.5}$Te$_{0.5}$ and the 115 reflection of CaF$_2$ in film C1. A 4-fold symmetry reflection is obtained as observed in the films on several oxide substrates, and we can identify the in-plane orientation as FeSe$_{0.5}$Te$_{0.5}$ [100] || CaF$_2$ [110]. It should be noted that the peak width of the 101 reflection is comparable to but not better than that reported in the film prepared on LaAlO$_3$ as shown in Fig. 1(c); FWHM of the peak is $\approx 1.0^\circ$ for C1 showing a larger value than reported for the film on LaAlO$_3$. Figure 1(d) shows the cross-sectional transmission electron microscopy (TEM) image of film C5 at the interface. Roughness of the boundary looks to be more emphasized when compared with the case of LaAlO$_3$ substrate, but no amorphous layer is observed between the film and the substrate.

The calculated c- and a-axis lengths are summarized in Fig. 1(e); the former is calculated from position of the 001–004 reflections, and the latter is determined from the position of 101 and the calculated c-axis length. The c-axis lengths of all the films exceed 5.94 Å, and are longer than that reported for the films grown on oxide substrates in our previous paper.$^{18,19}$ The a-axis lengths of three films show correspondingly short values, less than 3.78 Å, which are comparable with those reported by Bellingeri et al.$^{7}$ Thus, it is concluded that these films are compressed along the a-axis and are elongated simultaneously along the c-axis. Note that such a short a-axis length of the film is not due to a simple coincidence to the lattice parameters of CaF$_2$ ($a_0/\sqrt{2} = 3.863$ Å). The reason why the a-axis is so strongly compressed has not yet been clarified, and we can only speculate on a possible chemical reaction between FeSe$_{1-x}$Te$_x$ and F and/or some unknown mechanisms in FeSe$_{1-x}$Te$_x$ to shrink the a axis in oxygen-free environment.
TEM image at the interface of CaF$_2$ et al. significant benefits of using a CaF$_2$ than those in our previous works. 18,19)

Fig. 1. (a) X-ray diffractions of six FeSe$_x$Te$_{1-x}$ thin films grown on CaF$_2$(100). The origin of the vertical axis is shifted for each film. * indicates peaks from an aluminum holder. (b) Φ-scans of the 101 reflection of film C1 and the 115 reflection of CaF$_2$ substrate. (c) Comparison of the 101 reflections of film C1 with the films on LaAlO$_3$, and MgO in ref. 18. (d) Cross-sectional TEM image at the interface of CaF$_2$ and film C5. (e) c-axis length vs a-axis length of films C1, C3, and C5. The dashed line is a guide to the eye.

The temperature dependences of resistivity of the six films are summarized in Fig. 2(a). All the films exhibit a higher $T_c$ than those in our previous works. 18,19) $T_c$'s are concentrated within a narrow temperature region around 15 K with high reproducibility, even though the normal state resistivities are rather scattered. The observation of the less-scattered $T_c$'s shows a clear contrast to the results of the films on various oxide substrates. 18,19) Among the six films, C1 and C5 are remarkable for their $T_c$'s exceeding 14 K, which is the $T_c$ value reported for FeSe$_x$Te$_{1-x}$ single crystals in ambient pressure; the midpoint $T_c$ ($T_{\text{mid}}$) and zero-resistivity $T_c$ ($T_c(0)$) are 16.1 and 15.2 K for C1, and 16.3 and 15.3 K for C5, respectively. This is not the first example, and a higher $T_c$ (onset) of 21 K has been already reported by Bellingeri et al. 17) However, they have obtained such a high $T_c$ only in relatively thick films of 200 nm. We emphasize in the present study that even a far thinner film can exhibit a higher $T_c$ than bulk crystals, and we are sure that this is one of the significant benefits of using a CaF$_2$ oxygen-free substrate. In particular, when fabricating superconductor–normal metal–superconductor (SNS) Josephson junctions and superconductor–insulator–superconductor (SIS) tunnel junctions, it becomes very important to prepare a sharp interface between superconductors and normal metals and/or barrier insulators. For that purpose, thinner film have an advantage of smoother surfaces than thicker films, and we believe that CaF$_2$ will work as one of the promising substrates.

These films show remarkable properties also in a magnetic field. Figure 2(c) shows a suppression of $T_c$ by applying magnetic fields along the c-axis direction ($H \parallel c$). 20) Even under 14 T, the decrease of $T_{\text{mid}}$ is less than 2 K, and thus the upper critical field ($H_{c2}$) is suggested to be high. However, $H_{c2}$ at the region close to $T_c$ is not linear to $T$ suggesting that an application of the Werthamer–Helfand–Hohenberg (WHH) relation to the present case is invalid. With a simple application of the WHH relation to estimate $H_{c2}$ using $H_{c2}(0) = -0.69 T_c(dH_{c2}/dT)|_{T=T_c}$, we obtained $H_{c2} = 120$ T. This is obviously overestimated, and the actual $H_{c2}$ must be less than this value. However, even if we use a linear extrapolation of the tangential line at $H = 14$ T instead, and multiply 0.69 to the value at $T = 0$ K, we obtain $H_{c2} = 74.5$ T, which is still larger than those reported for FeSe$_{0.5}$Te$_{0.5}$ using $T_{\text{mid}}$ 21) and even using $T_{\text{onset}}$ 22) This result demonstrates the robustness of superconductivity in our FeSe$_{0.5}$Te$_{0.5}$ thin films under magnetic fields.

Finally, we evaluate the potential critical-current density of FeSe$_{0.5}$Te$_{0.5}$ for the application to thin-film conductors. The excellent properties observed in film C1 suggests that this film can show a high critical current density ($J_c$) in a superconducting state. We performed resistivity measure-
superconductivity has been recently confirmed in NdFeAs-(O,F) thin films prepared on the same substrate material, which indicates the common advantage of using CaF$_2$ to grow iron-based superconductor thin films.

**Acknowledgment** We thank D. Nakamura for technical assistance.

1) Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono: J. Am. Chem. Soc. 130 (2008) 3924.
2) H. Hiramatsu, T. Katase, T. Kamiya, M. Hirano, and H. Hosono: Appl. Phys. Lett. 93 (2008) 162504.
3) H. Hiramatsu, T. Katase, T. Kamoya, M. Hirano, and H. Hosono: Appl. Phys. Express 1 (2008) 101702.
4) E. Backen, S. Haindl, T. Niemeier, R. Hühne, T. Freudenberg, J. Werner, G. Behr, L. Schultz, and B. Holzapfel: Supercond. Sci. Technol. 21 (2008) 122001.
5) K. Iida, J. Hänisch, R. Hühne, F. Kurth, M. Kidszun, S. Haindl, J. Werner, L. Schultz, and B. Holzapfel: Appl. Phys. Lett. 95 (2009) 192501.
6) T. Kawaguchi, H. Uemura, T. Ohno, R. Watanabe, M. Tabuchi, T. Ujihara, K. Takenaka, Y. Takeda, and H. Ikuta: Appl. Phys. Express 2 (2009) 093002.
7) T. Kawaguchi, H. Uemura, T. Ohno, M. Tabuchi, T. Ujihara, K. Takenaka, Y. Takeda, and H. Ikuta: Appl. Phys. Lett. 97 (2010) 042509.
8) S. Takeda, S. Ueda, T. Yamagishi, S. Agatsuma, S. Takano, A. Mitsuda, and M. Naito: Appl. Phys. Express 3 (2010) 093101.
9) F. C. Hsu, J. Y. Luo, K. W. Yeh, T. K. Chen, T. W. Huang, P. M. Wu, Y. C. Lee, Y. L. Huang, Y. Y. Chu, D. C. Yan, and M. K. Wu: Proc. Natl. Acad. Sci. U.S.A. 108 (2011) 14262.
10) S. Margadonna, Y. Takabayashi, Y. Ohishi, Y. Mizuguchi, Y. Takan, T. Kageyama, T. Nakagawa, M. Takata, and K. Prassides: Phys. Rev. B 80 (2009) 064506.
11) S. Medvedev, T. M. McQueen, I. A. Troyan, T. Palasyuk, M. I. Erements, R. J. Cava, S. Naghavi, F. Casper, V. Kienonfohtov, G. Wortmann, and C. Felser: Nat. Mater. 8 (2009) 630.
12) M. K. Wu, F. C. Hsu, K. W. Yeh, T. W. Huang, J. Y. Luo, M. J. Wang, H. H. Chang, T. K. Chen, S. M. Rao, B. H. Mok, C. L. Chen, Y. L. Huang, C. T. Ke, P. M. Wu, A. M. Chang, C. T. Wu, and T. P. Peng: Physica C 469 (2009) 340.
13) Y. Han, W. Y. Li, L. X. Cao, S. Zhang, B. Xu, and R. R. Zhao: J. Phys.: Condens. Matter 21 (2009) 235702.
14) E. Bellingeri, R. Buzio, A. Gerbi, D. Marrè, S. Corgiu, M. R. Cimberle, M. Tropeano, A. S. Siri, A. Palenzona, and C. Feredehgini: Supercond. Sci. Technol. 22 (2009) 105007.
15) W. Si, Z. W. Liu, Q. Jie, W. G. Yin, J. Zhou, G. Gu, P. D. Johnson, and Q. Li: Appl. Phys. Lett. 95 (2009) 052504.
16) Y. Jam, R. Tanaka, T. Akiki, M. Hanawa, I. Tsukada, and A. Maeda: Jpn. J. Appl. Phys. 49 (2010) 023101.
17) E. Bellingeri, I. Pallecchi, R. Buzio, A. Gerbi, D. Marrè, M. R. Cimberle, M. Tropeano, M. Mutti, A. Palenzona, and C. Feredehgini: Appl. Phys. Lett. 96 (2010) 102512.
18) Y. Inami, T. Akiki, M. Hanawa, I. Tsukada, A. Ichinose, A. Maeda, T. Hikage, T. Kawaguchi, and H. Ikuta: Appl. Phys. Express 3 (2010) 043102.
19) M. Hanawa, A. Ichinose, I. Tsukada, Y. Inami, T. Akiki, T. Hikage, T. Kawaguchi, H. Ikuta, and A. Maeda: to be published in Jpn. J. Appl. Phys.
20) This sample is another six-terminal shape film simultaneously prepared on the same substrate of film C1 and named C2.
21) T. Klein, D. Brezziwatte, A. Demuer, W. Knafo, G. Lapertot, C. Marcenat, P. Rodière, I. Sheikin, P. Strobel, A. Sulpice, and P. Toulemonde: Phys. Rev. B 82 (2010) 184506.
22) V. Tsurkan, J. Deisenhofer, A. Günther, Ch. Kautz, H.-A. Krug von Nidda, K. Schmitt, and A. Loidl: arXiv:1006.4453v2.
23) K. Iida, S. Haindl, T. Thersleff, J. Hänisch, F. Kurth, M. Kidszun, R. Hühne, I. Mönch, L. Schultz, B. Holzapfel, and R. Heller: Appl. Phys. Lett. 97 (2010) 172507.
24) S. Lee, J. Jiang, Y. Zhang, C. B. Park, J. D. Weiss, C. Tarantini, C. T. Nelson, H. W. Jang, C. M. Folkman, S. H. Baek, A. Polianyski, D.Abraimov, A. Yamamoto, J. Park, W. X. Pan, E. H. Helstrom, D. C. Larbalestier, and C. B. Eom: Nat. Mater. 9 (2010) 397.
25) C. B. Eom, M. K. Lee, J. H. Chol, L. J. Belenky, X. Song, L. D. Cooley, M. T. Naus, S. Patrikkl, J. Jiang, M. Rikel, A. Polyanskii, A. Gurevich, X. Y. Cal, S. D. Bu, S. E. Babcock, E. E. Helstrom, D. C. Larbalestier, N. Rogado, K. A. Regan, M. A. Hayward, T. He, J. S. Slusky, K. Inumaru, M. K. Haas, and R. J. Cava: Nature 411 (2001) 558.