PHYSICAL REVIEW B **81**, 092506 (2010)

Superconductivity in epitaxial thin films of $Fe_{1.08}Te:O_x$

Weidong Si,[*] Qing Jie, Lijun Wu, Juan Zhou, Genda Gu, P. D. Johnson, and Qiang Li

Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York 11973, USA

(Received 20 November 2009; revised manuscript received 18 February 2010; published 12 March 2010)

Superconducting thin films of $Fe_{1.08}Te:O_x$ have been epitaxially grown on $SrTiO_3$ substrates by pulsed-laser deposition in controlled oxygen atmosphere. Although the bulk $Fe_{1.08}Te$ is not superconducting, thin films with oxygen are superconducting with an onset and a zero resistance transition temperature around 12 and 8 K, respectively. Oxygen was found to be crucial to the superconducting properties of these films, suggesting that the oxygen incorporation can induce superconductivity in FeTe thin films. A metal-insulator transition is found at about 60 K, lower than that of bulk (~70 K). From magnetoresistive measurements, we obtained the irreversibility line and the upper critical field.

DOI: 10.1103/PhysRevB.81.092506 PACS number(s): 74.78.−w, 74.62.Bf, 74.70.Ad

Superconductivity in ferropnictides has attracted much interest due to their high critical temperatures T_c and an unusual interplay of multiband superconductivity and antiferromagnetism mediated by the Fe ions in the itinerant antiferromagnetic parent compounds.[1] In the $Fe_{1+x}R_yTe_{1-y}$ ($R=Se,S$) family of materials, the parent compound $Fe_{1+x}Te$ is not a superconductor. A structural phase transition from tetragonal to monoclinic was found around 70 K and a metal-insulator transition occurs simultaneously with an antiferromagnetic metallic phase below the transition temperature.[2] The tetragonal β-phase $FeSe_x$ was found to be superconducting with a T_c of 8 K,[3] and 37 K under a pressure of 7 GPa.[4] T_c was raised to 14 K by 50% substitution of Se for Te.[5] S-substituted FeTe was also found to be superconducting around 10 K.[6] It was generally believed that the substitution of Se or S for Te destroys the antiferromagnetic phase and results in the superconducting phase.[6,7]

However, until now no superconductivity has been reported on oxygen-substituted $Fe_{1+x}Te$, although O, S, Se, and Te stay in the same column in the Periodic Table of elements. In fact, oxygen was considered detrimental to this class of materials, because most of the time it forms oxides with Fe and Te, instead of occupying the Te lattice sites.[8] On the other hand, it would be interesting to make thin films of $Fe_{1+x}Te$ on a cubic substrate. If the film could stick to the substrate with a tetragonal phase by the epitaxial strain, the antiferromagnetic phase transition may become weaker and the superconductivity may occur. In this Brief Report, we prepared epitaxial $Fe_{1.08}Te:O_x$ thin films on cubic $SrTiO_3$ (STO) substrates by pulsed-laser deposition (PLD). We found that the films made in the oxygen atmosphere are superconducting with an onset T_c (T_c^{onset}) around 12 K and a zero resistance T_c (T_c^0) about 8 K. The superconductivity is possibly due to the oxygen substitution, although other mechanisms may also play a role.

The target with nominal composition $Fe_{1.08}Te$ was prepared by solid-state reaction with appropriate stoichiometry of Fe and Te small chips and droplets. It is in a single phase as confirmed by x-ray diffraction. A KrF excimer laser (wavelength of 248 nm) was used for thin-film deposition with an energy density of ~3.0 J/cm^2 and a repetition rate of 5 Hz. The substrate temperature was varied from 300 °C to 450 °C. The oxygen pressure was kept below 1×10^{-4} Torr. After deposition, the films were cooled to room temperature at a rate of 60 °C/min. Structural characterization was performed using x-ray diffractometry and high-resolution transmission electron microscopy (HRTEM). Resistivity was measured by the standard four-probe method in a physical property measurement system (PPMS, Quantum Design) and magnetization was measured in a superconducting quantum interference device (magnetic property measurement system (MPMS), Quantum Design) with an ultralow-field option.

Figure 1(a) shows a θ-2θ x-ray diffraction scan for a typical 1000 Å $Fe_{1.08}Te:O_x$ film grown on a (100) STO substrate. Only the (00l) peaks from the film and substrate are present indicating that the out-of-plane alignment of the film is good. Figures 1(b) and 1(c) show the ϕ scan of (112) peak from the thin film and the substrate. Both have four peaks with 90° intervals showing fourfold symmetry. Peaks from the thin film and the substrate are well aligned with each other, indicating that the film is aligned in plane, too. We estimate that the lattice constants a and c of the film are about 3.821 and 6.275 Å. These values are quite similar to that of bulk,[7] although the film is in quite strong tensile strain on STO substrates, which are cubic with a lattice constant of 3.905 Å. The strain may be relieved at the interface because of the relatively large lattice mismatch. Figure 2 shows a cross-sectional HRTEM image of the $Fe_{1.08}Te:O_x$ film on a STO substrate. The film is epitaxially grown on the substrate with the c axis along the substrate normal. Energy-dispersive x-ray spectroscopy shows that the films have a composition close to the nominal composition of the target.

Figure 3 shows the temperature dependence of resistivity of $Fe_{1.08}Te:O_x$ thin films. The film shows semiconductor behavior above ~60 K, which is consistent with the bulk materials. Below 60 K, a gradual crossover to metallic behavior was found, corresponding to the structural phase transition observed in the bulk around 70 K. Detailed measurement shows that, within 2 or 3 days, this crossover becomes less sharp and its temperature increases to near 70 K, about the same as that of the bulk, although not much change was found in its superconducting properties. The metallic behavior persists down to about 15 K, then resistance shows a small upturn before dropping to zero. In the case of the bulk materials, it is almost flat down to zero temperature.[7] Figure 3 inset shows the resistive superconducting transition of two

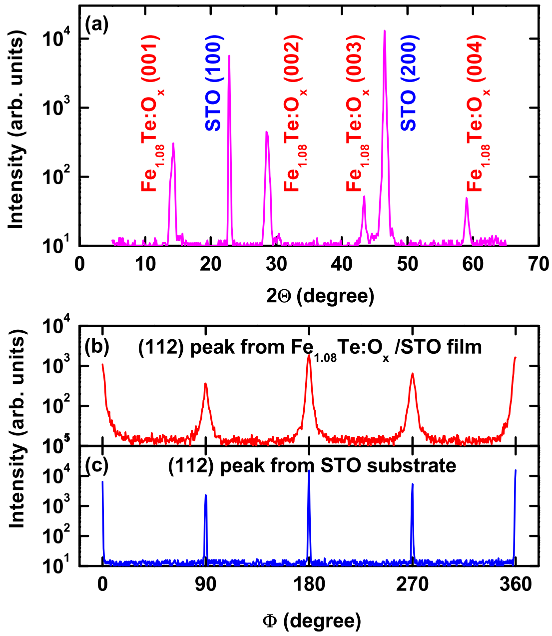

FIG. 1. (Color online) (a) θ-2θ scan of an $Fe_{1.08}Te:O_x$ thin film on a (100) STO substrate. (b) ϕ scan of the (112) peak from the $Fe_{1.08}Te:O_x$ film and (c) from the STO substrate.

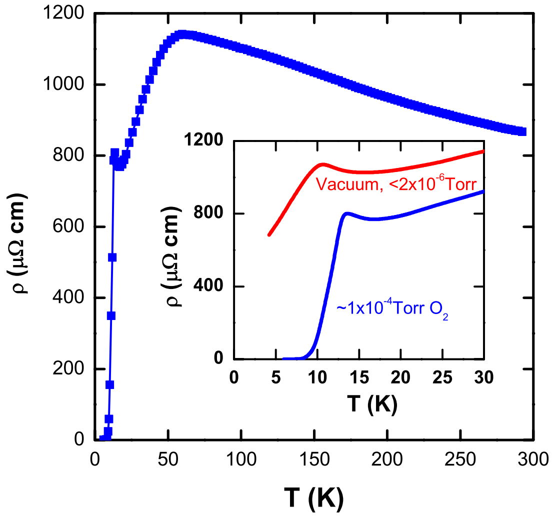

FIG. 3. (Color online) Temperature dependence of resistivity of one $Fe_{1.08}Te:O_x$ thin film grown on a STO substrate. The inset shows the resistive superconducting transition of two $Fe_{1.08}Te$ films made with oxygen and in vacuum.

films. One was made in oxygen with a clear zero resistance. The other was made in "vacuum" (less than 2×10^{-6} Torr at elevated temperature; the base pressure of our PLD system is about 2×10^{-7} Torr). Its resistivity also shows a drop at low temperature but does not go to zero. This indicates that oxygen is crucial to the superconducting properties of the $Fe_{1.08}Te:O_x$ thin films.

Figure 4 shows the temperature dependence of the magnetization of an $Fe_{1.08}Te:O_x$ thin film during the superconducting transition in zero-field cooling (ZFC) and field cooling (FC) under 2 Oe magnetic field along the *c*-axis direction. A strong diamagnetic signal was observed in ZFC around 5 K, which is a little lower than the zero resistance T_c determined from the resistivity measurement. The strong magnetic shielding effect clearly demonstrates the bulk nature of the superconductivity in the sample. Figure 4 inset shows the temperature dependence of the magnetization of the superconducting $Fe_{1.08}Te:O_x$ thin film with the STO substrate in a magnetic field of 0.5 T. The large tail at low temperature comes from the paramagnetic response of the substrate. A peak around 50 K was found and is probably associated with the antiferromagnetic transition observed in the bulk. No anomaly was found around 125 K, as observed by Fang *et al.*[5]

We also performed the magnetoresistive measurement of our samples under different magnetic fields along the *c* axis across the superconducting transition. The results are shown in Fig. 5(a). Under magnetic fields, broadening of the transition was observed. The same data are plotted in a semilogarithmic scale in Fig. 5(b). The resistivity drops, accelerating as the temperature decreases, about five orders of magnitude from the normal-state value to the level below the resolution of our measurement. We define $T_c^{onset}(H)$ as the intersection by extrapolating both the normal resistance and the super-

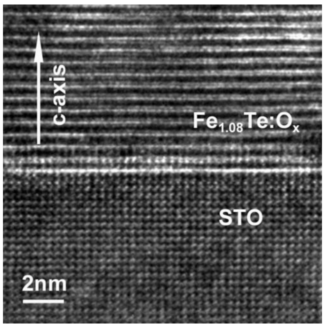

FIG. 2. Cross-section HRTEM image of an $Fe_{1.08}Te:O_x$ thin film on a STO substrate.

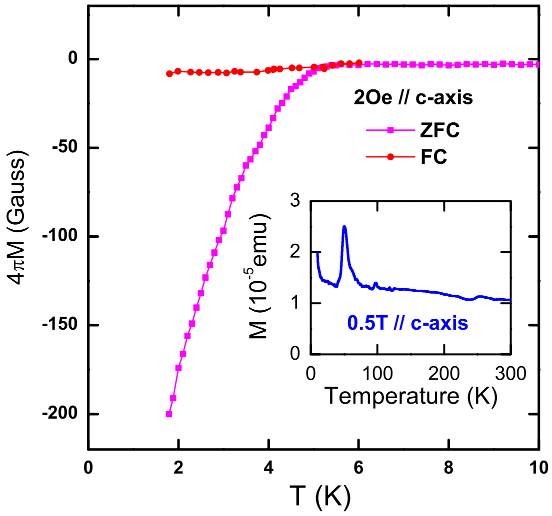

FIG. 4. (Color online) Magnetic superconducting transition of one $Fe_{1.08}Te:O_x$ thin film grown on a STO substrate in ZFC and FC. Inset shows the magnetization versus temperature measurement from 10 K to room temperature.

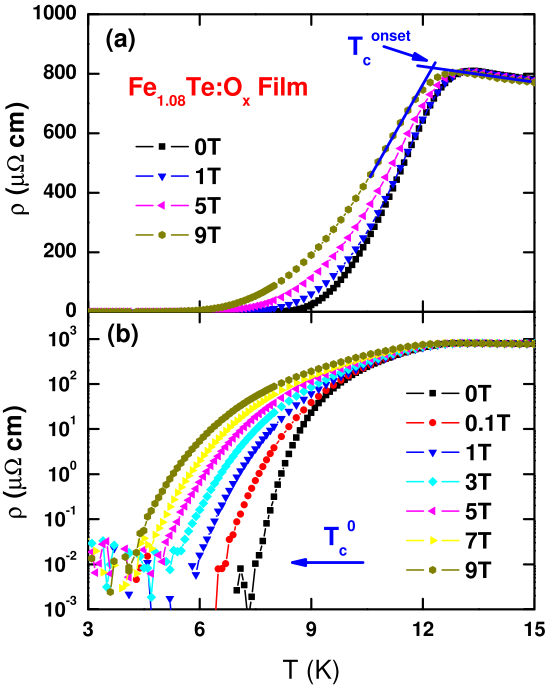

FIG. 5. (Color online) (a) Superconducting transition under various magnetic fields along the c axis. For clarity, data taken under 0.1, 3, and 7 T fields are not shown; (b) all data are shown in semilogarithmic scale.

conducting transition line, as shown in Fig. 5(a), and $T_c^0(H)$ as the temperature where resistance drops below our measuring resolution ($\sim$50 nV/cm), as shown in Fig. 5(b). The irreversibility line $H_{irr}(T)$ and the upper critical field $H_{c2}(T)$ are obtained from T_c^0 and T_c^{onset}, respectively. The results are shown in Fig. 6. $H_{irr}(T)$ is obtained using critical current density criteria of 100 A/cm^2 at an electrical field sensitivity of 50 nV/cm.[9] By using the Werthamer-Helfand-Hohenberg model,[10] $-H_{c2}(0)=0.7T_c dH_{c2}/dT|_{T_c}$, we estimated $H_{c2}(0)$ to be $\sim$200 T from T_c^{onset}. Although this value is probably overestimated, the actual $H_{c2}(0)$ can be remarkably high. Considering the fairly low T_c in this system with other high T_c superconductors, this is a especially striking property of the "11" system.[11]

As shown in Fig. 3 inset, the oxygen is found to be crucial to the superconducting properties of the $Fe_{1.08}Te:O_x$ thin films. All films with a clear zero resistance were made with oxygen. Although the films made in "vacuum" also show a sharp decrease in resistance below 10 K, their resistances never reach zero down to 1.8 K. Since there is always residual gas in the chamber even in this vacuum, these films may still have oxygen, although with much less amount. Thus, it is reasonable to believe that superconductivity in our $Fe_{1.08}Te:O_x$ film is due to the oxygen substitution of Te, similar to the superconductivity from the Se and S substitutions of Te in FeTe.[6] In addition, the lower crossover temperature from the semiconductor to metallic behavior in our superconducting films is also an indicator of the oxygen substitution.[6] However, it is interesting to note some drawbacks in this simple explanation. First, oxygen has a much smaller radius than Te; therefore, oxygen-substituted FeTe should have smaller lattice constants, but our observation shows a very small change. Second, a large amount of oxygen substitution for Te is not stable since it most likely forms different oxides with Fe and Te.[8] For example, if the oxygen pressure is larger than 1×10^{-4} Torr in the growth chamber, no epitaxial film of FeTe would grow. Although the exact oxygen content in our films is unknown, it is quite likely that there is no large amount of oxygen in the films from our observation of the lattice constant change. It is then difficult to comprehend that a small amount of oxygen substitution can make the film superconducting.

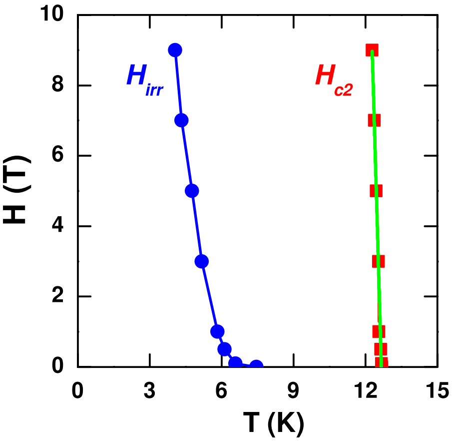

FIG. 6. (Color online) Irreversibility field H_{irr} and upper critical field H_{c2} obtained from T_c^0 and T_c^{onset}. The straight line is a linear fitting for $H_{c2}(T)$, which gives $dH_{c2}/dT\sim-23$ T/K.

One possible scenario is that a phase separation occurs at low temperature. Some parts of the film are superconducting and some other parts are antiferromagnetic metal as in the bulk. Phase separation may be static and there are oxygen-rich and oxygen-poor regions. It may also be electronic which do not have separated chemical phases and is much harder to detect. The simultaneous observation of the antiferromagnetic phase transition and superconductivity in our thin films is consistent with this interpretation. This behavior has also been observed in $SmFeAsO_{1-x}F_x$ (Ref. 12) and $Ba_{1-x}K_xFe_2As_2$.[13] Another possible factor may be the epitaxial strain, which may stabilize the high-temperature tetragonal phase and weaken the antiferromagnetic phase transition, therefore making the superconductivity easier to occur. We would like to point out that it is important to know whether oxygen stays in the lattice site or not. If it is in the interstitial sites, there might be a complete different interpretation of its superconducting origin. For example, excess Fe in Fe(2) lattice sites is known to create localized magnetic moments, which cause pair breaking and destroy the superconductivity. Oxygen in the chamber may reduce the amount of excess Fe by forming secondary oxides with Fe, thus making superconductivity more favorable. It is noteworthy that moisture has recently been observed to cause superconductivity in $FeTe_{0.8}S_{0.2}$, which may be due to the same mechanism.[14] Further study is needed in clarifying this issue.

In conclusion, we have grown epitaxial $Fe_{1.08}Te:O_x$ thin films in controlled oxygen atmosphere by pulsed-laser deposition. Thin films are superconducting with an onset T_c of about 12 K. Oxygen was found to be crucial to the superconducting properties of these films. A metal-insulator transition is found at about 60 K, lower than that of bulk. The upper critical field $H_{c2}(0)$ was found to be remarkably high considering its moderate T_c.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Science, under Contract No. DE-AC02-98CH10886.

---

*wds@bnl.gov

[1] K. Ishida, Y. Nakai, and H. Hosono, J. Phys. Soc. Jpn. **78**, 062001 (2009).

[2] S. Li, C. de la Cruz, Q. Huang, Y. Chen, J. W. Lynn, J. Hu, Yi-L. Huang, F.-C. Hsu, K.-W. Yeh, M.-K. Wu, and P. Dai, Phys. Rev. B **79**, 054503 (2009).

[3] Fong-Chi Hsu, Jiu-Yong Luo, Kuo-Wei Yeh, Ta-Kun Chen, Tzu-Wen Huang, Phillip M. Wu, Yong-Chi Lee, Yi-lin Huang, Yan-Yi Chu, Der-Chung Yan, and Maw-Kuen Wu, Proc. Natl. Acad. Sci. U.S.A. **105**, 14262 (2008).

[4] S. Margadonna, Y. Takabayashi, Y. Ohishi, Y. Mizuguchi, Y. Takano, T. Kagayama, T. Nakagawa, M. Takata, and K. Prassides, Phys. Rev. B **80**, 064506 (2009).

[5] M. H. Fang, H. M. Pham, B. Qian, T. J. Liu, E. K. Vehstedt, Y. Liu, L. Spinu, and Z. Q. Mao, Phys. Rev. B **78**, 224503 (2008).

[6] Yoshikaza Mizuguchi, Fumiaki Tomioka, Shunsuke Tsuda, Takahide Yamaguchi, and Yoshihiro Takano, Appl. Phys. Lett. **94**, 012503 (2009).

[7] B. C. Sales, A. S. Sefat, M. A. McGuire, R. Y. Jin, D. Mandrus, and Y. Mozharivskyj, Phys. Rev. B **79**, 094521 (2009).

[8] T. M. McQueen, Q. Huang, V. Ksenofontov, C. Felser, Q. Xu, H. Zandbergen, Y. S. Hor, J. Allred, A. J. Williams, D. Qu, J. Checkelsky, N. P. Ong, and R. J. Cava, Phys. Rev. B **79**, 014522 (2009).

[9] Qiang Li, M. Suenaga, T. Kaneko, K. Sato, and Ch. Simmon, Appl. Phys. Lett. **71**, 1561 (1997).

[10] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 295 (1966).

[11] Weidong Si, Zhi-Wei Lin, Qing Jie, Wei-Guo Yin, Juan Zhou, Genda Gu, P. D. Johnson, and Qiang Li, Appl. Phys. Lett. **95**, 052504 (2009).

[12] A. J. Drew, Ch. Niedermayer, P. J. Baker, F. L. Pratt, S. J. Blundell, T. Lancaster, R. H. Liu, G. Wu, X. H. Chen, I. Watanabe, V. K. Malik, A. Dubroka, M. Rossle, K. W. Kim, C. Baines, and C. Bernhard, Nature Mater. **8**, 310 (2009).

[13] J. T. Park, D. S. Inosov, Ch. Niedermayer, G. L. Sun, D. Haug, N. B. Christensen, R. Dinnebier, A. V. Boris, A. J. Drew, L. Schulz, T. Shapoval, U. Wolff, V. Neu, X. Yang, C. T. Lin, B. Keimer, and V. Hinkov, Phys. Rev. Lett. **102**, 117006 (2009).

[14] Y. Mizuguchi, K. Deguchi, S. Tsuda, T. Yamaguchi, and Y. Takano, arXiv:0912.2240 (unpublished).