Interface superconductivity in FeSe on SrTiO$_3$ thin films grown by the PLD technique

T Kobayashi, H Ogawa, F Nabeshima, and A Maeda
Dept. of Basic Science, University of Tokyo, Meguro, 153-8902, Tokyo, Japan
E-mail: kobayashi-tomoki375@g.ecc.u-tokyo.ac.jp

Abstract. In this study, we fabricate 7–25-nm-thick films of FeSe/STO using pulsed laser deposition (PLD). The grown films exhibit superconductivity with an onset $T_c$ that is much higher than that of bulk FeSe under ambient pressure. The observed $T_c$ values are exceptionally high in terms of the strain vs. $T_c$ relationship of the same material established so far. Furthermore, $T_c$ increases as the film thickness decreases. This is in good agreement with the results reported for films grown by molecular beam epitaxy (MBE) that exhibit interface superconductivity. These results indicate the realization of interface superconductivity in PLD-grown FeSe/STO. Furthermore, our PLD technique requires no post-annealing to realize interface superconductivity, which is different from MBE techniques. Because the PLD technique has the advantage that various interfaces can be fabricated easily by simply altering the target materials, our results open novel routes to study interface superconductivity toward higher $T_c$ by systematic control of the interface.
1. Introduction

The iron chalcogenide superconductor FeSe has garnered significant attention for its high tunability of the superconducting transition temperature \( T_c \). Although the onset \( T_c^{\text{onset}} \) of bulk FeSe is 9 K at ambient pressure \([1]\), it is highly enhanced by various methods. For instance, \( T_c^{\text{onset}} \) increases to 38 K by applying hydrostatic pressure \([2, 3]\). The doping of electrons by intercalation \([4, 5]\) or the electric field effect \([6, 7, 8, 9, 10, 11, 12]\) increases \( T_c^{\text{onset}} \) to 50 K. In particular, zero resistivity below 46 K is realized in \([11, 12]\). Furthermore, angle-resolved photoemission spectroscopy (ARPES) measurements reported that a monolayer FeSe film on SrTiO\(_3\) (STO) \([13, 14]\) exhibited gap opening at the Fermi level below 65 K, which has been interpreted as a manifestation of superconductivity. The \( T_c \) enhancement in monolayer FeSe on STO (FeSe/STO) is attributed to interfacial effects, such as electron doping from the STO substrate \([15]\) and electron-phonon interaction with phonons of STO \([16]\). Thus, the superconductivity in FeSe/STO is expected to be the first interface-enhanced superconductivity, where the existence of the interface plays a crucial role \([17, 18]\).

In contrast to the ARPES results, resistivity measurements reported a \( T_c^{\text{onset}} \) of 40–45 K \([13, 19, 20]\) and a much lower zero-resistance temperature \( T_c^{\text{zero}} \), and these are lower than those of electron-doped FeSe systems \([11, 12]\). This discrepancy in the reported values of \( T_c \) observed by different measurement techniques suggests that the exact feature of interface superconductivity in FeSe/STO is still far from being fully understood. Therefore, a more detailed investigation of the interfacial effects is essential. In this context, the artificial control of the interface is a promising approach. For feasible control of the interface, pulsed laser deposition (PLD) has advantages in fabricating various heterostructures at low cost because different materials can be deposited by simply switching the target materials. However, all studies on the interface superconductivity of FeSe published so far were performed using the molecular beam epitaxy (MBE) technique. This is because it is difficult to grow high-quality thin films of compounds that contain highly volatile Se using other growth techniques. Indeed, none of the previous studies by PLD succeeded in fabricating FeSe films that exhibited the interface superconductivity.

In this paper, we report the successful growth of FeSe/STO which exhibits interface superconductivity, using the PLD technique for the first time. We fabricate 7–25-nm-thick FeSe films on atomically flat STO substrates. The grown films exhibit a \( T_c^{\text{onset}} \) higher than 20 K, which is much higher than that of bulk FeSe \([1]\). The enhanced \( T_c \) cannot be explained in terms of the in-plane strain effect on the bulk superconductivity of FeSe \([21, 22, 23, 24]\). \( T_c \) increases with decreasing film thickness, which is in good agreement with those reported for MBE-grown FeSe/STO \([23, 24]\). These results suggest that we realized interface superconductivity in FeSe/STO, grown using the PLD technique for the first time.
2. Experimental methods

All the FeSe thin films in this study were grown on insulating STO (001) substrates using PLD with a KrF laser. Prior to deposition, the STO substrate was annealed at 1000°C in air and rinsed with water to obtain a TiO$_2$-terminated surface with a step-terrace structure [27] (figure 1(a)). Reflection high-energy electron diffraction (RHEED) images of the substrates exhibited the (2 × 1) reconstructed patterns [13] under vacuum at a growth temperature of 500°C (figure 1(b)). Films were deposited by ablating the Fe$_{1.1}$Se target [21] at a growth rate of 0.2–0.5 nm/min. The RHEED patterns of the grown films displayed streaks, indicating a flat surface of the films (figure 1(c)). Because RHEED oscillation in FeSe/STO was sometimes not observed in this study, the RHEED intensity of the films on LaAlO$_3$, which were grown simultaneously as the films on STO, was observed during the deposition to control the film thickness. Below, we present a series of four samples with different thicknesses of 7, 10, 16, and 25 nm, as typical representatives.

The orientation and crystal structure of the grown films were characterized using X-ray diffraction (XRD) measurements with Cu Kα radiation at room temperature. The thicknesses of the films were estimated from the Laue fringe around the (001) reflection peak or using a Dektak 6M stylus profiler. Resistivity was measured using a physical property measurement system (PPMS), from 2 to 200 K.

3. Results and discussion

Figure 2(a) illustrates the XRD patterns of four films with different thicknesses. All the films indicated only the (00l) reflection peaks of tetragonal FeSe, except for the peaks derived from the substrates and Ag paste attached to the films for the resistivity measurement. These results indicate the single-phase nature of FeSe and c-axis orientation of the films. Figure 2(b) illustrates an enlarged plot of the (001) reflection peaks. All the films showed clear Laue fringes, indicating a flat surface. Figure 2(c) illustrates the rocking curves of the (001) reflection peaks of the films. All films showed a full width at half maximum (FWHM) smaller than 0.16°, indicating high crystalline quality. All the films were under tensile strain with their a-axis constant larger than 3.81 Å (cf. bulk FeSe has $a = 3.77$ Å). The structural properties of the films are summarized in table 1.

| Sample | Thickness (nm) | $a$ (Å) | $c$ (Å) | $T_{\text{onset}}$ (K) | $T_{\text{zero}}$ (K) |
|--------|---------------|---------|---------|----------------|----------------|
| #1     | 7             | 3.81    | 5.48    | 28             | 17             |
| #2     | 10            | 3.82    | 5.47    | 30             | 19             |
| #3     | 16            | 3.83    | 5.47    | 28             | 17             |
| #4     | 25            | 3.82    | 5.48    | 23             | 13             |

Table 1. Characteristics of the grown films.
Figures 3(a) and (b) illustrate the temperature dependence of resistivity $\rho(T)$ of the films. All films exhibited a metallic behavior. The 7-nm-thick film exhibited a higher resistivity than the other films possibly because of the deterioration caused by air exposure. Remarkably, all samples exhibited a superconducting transition with a $T_{c}^{\text{onset}}$ higher than 20 K. These $T_{c}^{\text{onset}}$ values were much higher than those of the bulk at ambient pressure. Furthermore, $T_{c}$ increased as the thickness of the films decreased, except for the 7-nm-thick film, as will be discussed later.

It is well known that in-plane strain strongly affects the superconducting properties of FeSe [21, 22, 24, 23]. FeSe thin films under compressive strain exhibit enhanced $T_{c}^{\text{onset}}$ up to 12 K when $\epsilon \equiv (a_{\text{film}} - a_{\text{bulk}})/a_{\text{bulk}} < -1.0\%$ [22], where $a_{\text{film}}$ and $a_{\text{bulk}}$ are the $a$-axis constants of the films and bulk [28], respectively. However, tensile strain decreases $T_{c}$ and completely suppresses superconductivity when $\epsilon$ is greater than $+0.6\%$ [22]. Similar results were obtained in subsequent studies on bulk crystals [24, 23]. We plot $T_{c}^{\text{onset}}$ of the films grown in this study in the strain-vs-$T_{c}^{\text{onset}}$ plot [22] in figure 3(c). The present data largely deviate from the well-established strain-$T_{c}$ relation. The $\epsilon$ values in the grown films, which are higher than 0.9%, should lead to non-superconductivity, according to the strain-$T_{c}$ relation. Thus, these high $T_{c}$ values cannot be explained by the established strain effect. This result suggests that interface effects are responsible for the high $T_{c}$ of the films.

The interface superconductivity in the grown films is also suggested by the thickness
dependence of $T_{c\text{onset}}$ (figure 3(d)). Except for the 7-nm-thick film, $T_{c\text{onset}}$ increases as the thickness of the film decreases, as aforementioned. This negative correlation between the film thickness and $T_c$ is in good agreement with the results obtained for MBE-grown FeSe/STO, which exhibited interface superconductivity [25, 26]. The negative correlation between film thickness and $T_c$ was interpreted as follows [25]: Because FeSe layers apart from the interface are considered not to be subject to interfacial effects [13], it is likely that the very thin layer in the vicinity of the interface becomes superconducting. When the thickness of the film is increased, the number of doped electrons at the superconductive interface of FeSe/STO is reduced, which results in a reduction of $T_c$. Although the validity of this interpretation is still open, the results of the thickness dependence, together with the extraordinarily high $T_c$ in terms of the
strain-$T_c$ relation indicate the interface superconductivity in the films grown on STO. Note that the thickness dependence of $T_c$ is in sharp contrast to that of FeSe thin flakes \cite{29, 30, 31} and FeSe on bilayer graphens \cite{32}, where $T_c$ decreases as the thickness decreases. This difference is consistent with the fact that the interface between FeSe and STO plays a crucial role in realizing enhanced superconductivity in the grown films.

Compared with MBE-grown films \cite{25, 26}, all films other than the 7-nm-thick sample exhibited approximately the same value of $T_c^{\text{onset}}$ (figure 3(d)). Remarkably, our films exhibited a high $T_c$ without post-annealing. MBE growth requires a post-annealing process to remove excess Se \cite{33} which suppresses the superconductivity. The excess Se is due to the Se-rich growth conditions of the MBE techniques. However, approximately the same composition is transferred from the Fe$_{1.1}$Se target to a film during PLD growth, which results in much less excess Se in the grown film. This feature of the PLD technique enables us to obtain a superconducting FeSe/STO without post-annealing, which is different from MBE.

**Figure 3.** (a), (b) Temperature dependence of the resistivity of the grown films. (c) $T_c^{\text{onset}}$ as a function of strain of the films together with the data in \cite{22}. (d) Thickness dependence of $T_c^{\text{onset}}$ of the films. Data for the films grown by MBE \cite{25} are also plotted (black triangles).
The 7-nm-thick film exhibited a lower $T_c$ than the 10-nm-thick film, possibly owing to degradation by air exposure. Thus, deposition with a protection layer is necessary for films thinner than 10 nm to obtain a higher $T_c$, which is now under way.

4. Conclusion

In conclusion, we fabricated FeSe films on STO with a thickness of 7–25 nm which exhibited superconductivity with $T_{\text{onset}}$ much higher than that of bulk FeSe under ambient pressure. The observed $T_c$ in all the films was exceptionally high in terms of the strain-$T_c$ relation of the same material established so far. $T_c$ increased with decreasing film thickness, which is in good agreement with that of MBE-grown films that exhibited interface superconductivity [25, 26]. These results indicate that we successfully realized interface superconductivity in PLD-grown FeSe/STO. Furthermore, the PLD growth method has the advantage of realizing interface superconductivity without post-annealing, which is different from MBE techniques. PLD has the advantage of fabricating various heterostructures because different materials can be deposited by simply changing the target materials. Thus, our results accelerate a study of interface superconductivity toward higher $T_c$ by systematically controlling the interface.

Acknowledgments

We would like to acknowledge K. Ueno and H. Okuma at the University of Tokyo for their technical support of the XRD and AFM measurements.

References

[1] Hsu F C, Luo J Y, Yeh K W, Chen T K, Huang T W, Wu P M, Lee Y C, Huang Y L, Chu Y Y, Yan D C and Wu M K 2008 Proceedings of the National Academy of Sciences 105 14262–14264 ISSN 0027-8424 (Preprint https://www.pnas.org/content/105/38/14262.full.pdf) URL https://www.pnas.org/content/105/38/14262
[2] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2008 Appl. Phys. Lett. 93(15) 152505
[3] Sun J P, Matsuura K, Ye G Z, Mizukami Y, Shimozawa M, Matsubayashi K, Yamashita M, Watashigai T, Kasahara S, Matsuda Y, Yan J Q, Sales B C, Uwatoko Y, Cheng J G and Shibauchi T 2016 Nat. Commun 7 12146
[4] Guo J, Jin S, Wang G, Wang S, Zhu K, Zhou T, He M and Chen X 2010 Phys. Rev. B 82(18) 180520 URL https://link.aps.org/doi/10.1103/PhysRevB.82.180520
[5] Shi M Z, Wang N Z, Lei B, Ying J J, Zhu C S, Sun Z L, Cui J H, Meng F B, Shang C, Ma L K and Chen X H 2018 New Journal of Physics 20 123007 URL https://doi.org/10.1088/1367-2630/aaf312
[6] Lei B, Cui J H, Xiang Z J, Shang C, Wang N Z, Ye G J, Luo X G, Wu T, Sun Z and Chen X H 2016 Phys. Rev. Lett. 116(7) 077002 URL https://link.aps.org/doi/10.1103/PhysRevLett.116.077002
[7] Shiogai J, Ito Y, Mitsuhashi T, Nojima T and Tsukazaki A 2016 Nature Physics 12(1) 42 URL https://doi.org/10.1038/nphys3530
[28] McQueen T M, Huang Q, Ksenofontov V, Felser C, Xu Q, Zandbergen H, Hor Y S, Allred J, Williams A J, Qu D, Checkelsky J, Ong N P and Cava R J 2009 Phys. Rev. B 79(1) 014522 URL https://link.aps.org/doi/10.1103/PhysRevB.79.014522

[29] Schneider R, Zaitsev A G, Fuchs D and v Löhneysen H 2012 Phys. Rev. Lett. 108(25) 257003 URL https://link.aps.org/doi/10.1103/PhysRevLett.108.257003

[30] Farrar L S, Bristow M, Haghighirad A A, McCollam A, Bending S J and Coldea A I 2020 npj Quantum Materials 5 29 ISSN 2397-4648 URL https://doi.org/10.1038/s41535-020-0227-3

[31] Zhu C S, Lei B, Sun Z L, Cui J H, Shi M Z, Zhuo W Z, Luo X G and Chen X H 2021 Phys. Rev. B 104(2) 024509 URL https://link.aps.org/doi/10.1103/PhysRevB.104.024509

[32] Song C L, Wang Y L, Jiang Y P, Li Z, Wang L, He K, Chen X, Ma X C and Xue Q K 2011 Phys. Rev. B 84(2) 020503 URL https://link.aps.org/doi/10.1103/PhysRevB.84.020503

[33] Zhang W, Li Z, Li F, Zhang H, Peng J, Tang C, Wang Q, He K, Chen X, Wang L, Ma X and Xue Q K 2014 Phys. Rev. B 89(6) 060506 URL https://link.aps.org/doi/10.1103/PhysRevB.89.060506