Letter

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

T Kobayashi*, H Ogawa, F Nabeshima and A Maeda

Department of Basic Science, University of Tokyo, Meguro 153-8902, Tokyo, Japan

E-mail: kobayashi-tomoki375@g.ecc.u-tokyo.ac.jp

Received 2 March 2022, revised 29 April 2022
Accepted for publication 5 May 2022
Published 8 June 2022

Abstract

In this study, we fabricate 5–30 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, except for films thinner than 10 nm. This thickness dependence of $T_c$ 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.

Supplementary material for this article is available online

Keywords: iron-based superconductor, interface superconductivity, thin-film growth

(Some figures may appear in colour only in the online journal)

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 $T_c$ ($T_{c\text{onset}}$) 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 [6–12] increases $T_{c\text{onset}}$ to 50 K.

* Author to whom any correspondence should be addressed.

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 $T_{\text{onset}}$ of 40–45 K [13, 19, 20] and a much lower zero-resistance temperature ($T_{\text{c}}$), and these are lower than those of electron-doped FeSe systems [11, 12]. This discrepancy in the reported values of $T_{\text{c}}$ 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 5–30 nm thick FeSe films on atomically flat STO substrates. The grown films exhibit a $T_{\text{c}}$ higher than 19 K, which is much higher than that of bulk FeSe [1]. The enhanced $T_{\text{c}}$ cannot be explained in terms of the in-plane strain effect on the bulk superconductivity of FeSe [21–24]. Except for films thinner than 10 nm, $T_{\text{c}}$ increases with decreasing film thickness. This thickness dependence of $T_{\text{c}}$ is in good agreement with those reported for MBE-grown FeSe/STO [25, 26]. 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. 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)), which is essential to realize interface superconductivity in FeSe/STO using PLD. Prior to deposition, the substrate was then kept for 2 hours at a growth temperature of 500 °C. Reflection high-energy electron diffraction (RHEED) images of the substrates exhibited the $(2 \times 1)$ reconstructed patterns [13] under vacuum at the growth temperature. Films were deposited by ablating the Fe$_1.1$Se target [21] at a growth rate of 0.2–0.5 nm min$^{-1}$. The laser repetition rate was 1–5 Hz and the target-to-substrate distance was 50 mm. 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.

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 $c$-axis and $a$-axis lengths of the films were estimated from $(00l)$ $(l = 1, 2, 3$, and $4)$, $(\pm 204)$, and $(0 \pm 24)$ reflections using 2θ-ω scans. 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 representative 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 resistivity measurement. These results indicate the single-phase nature of FeSe and $c$-axis orientation of the films. In addition, we confirmed the in-plane alignment of the films as FeSe [100]/STO [100]. 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 smaller than 0.16°, indicating high crystalline quality. All the films were under tensile strain with their $a$-axis constant larger than 3.79 Å (cf bulk FeSe has $a = 3.77$ Å). The structural properties of the films are summarized in table 1.

Figures 3(a) and (b) illustrate the temperature dependence of resistivity $\rho(T)$ of the films. All films exhibited a metallic behavior. Remarkably, all samples exhibited a superconducting transition with a $T_{\text{onset}}$ higher than 20 K. These $T_{\text{onset}}$ values were much higher than those of the bulk at ambient pressure.

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

The interface superconductivity in the grown films is also suggested by the thickness dependence of $T_{\text{onset}}$. Figure 4(a) shows $T_{\text{onset}}$ as a function of film thickness $d$ for all the films grown in this study. In the case of films with $d \geq 10$ nm, $T_{\text{onset}}$
Figure 1. (a) Atomic force microscope topographic image of an STO substrate after the surface treatment. Clear step terrace structures are observed. (b) RHEED image of an STO substrate just before the deposition. (c) RHEED image of a grown FeSe film.

Figure 2. (a) XRD patterns of the grown films. Asterisk represents reflections from Ag paste. (b) Enlarged plot around the (001) reflections. (c) Rocking curves of the (001) peaks of the grown films.
Table 1. Characteristics of the grown films. $d$ represents the film thickness.

| Sample | $d$ (nm) | $a$ (Å)       | $c$ (Å)       | $T_{c\text{onset}}$ (K) | $T_{c\text{zero}}$ (K) |
|--------|----------|---------------|---------------|------------------------|------------------------|
| #1     | 7        | 3.808 ± 0.009 | 5.485 ± 0.006 | 28                     | 17                     |
| #2     | 10       | 3.814 ± 0.002 | 5.472 ± 0.002 | 30                     | 19                     |
| #3     | 16       | 3.816 ± 0.002 | 5.467 ± 0.002 | 28                     | 17                     |
| #4     | 25       | 3.794 ± 0.004 | 5.483 ± 0.003 | 23                     | 13                     |

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 [22].

Figure 4. (a) Thickness dependence of $T_{c\text{onset}}$ of the films. Data for the films grown by MBE [25] are also plotted (black triangles). (b) Thickness dependence of resistivity at 200 K of the films. $\rho(200\text{ K})$ increases as the thickness decreases. 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 [29, 30] and FeSe on bilayer graphenes [31], 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 [25, 26], all films with $d \geq 10$ nm exhibited approximately the same value of $T_{c\text{onset}}$ (figure 4(a)). Remarkably, our films exhibited a high $T_c$ without post-annealing. MBE growth requires a post-annealing process to remove excess Se [32] 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.

The PLD-grown films with $d < 10$ nm did not show a significant increase in $T_{c\text{onset}}$ as the film thickness decreased, different from the MBE-grown films, and the 5 nm thick film did not even exhibit superconductivity.
Figure 4(b) illustrates resistivity at 200 K for all samples. For \( d \geq 10 \) nm, resistivity tends to decrease as the thickness decreases, possibly due to the existence of carrier-doped interfaces. However, for \( d < 10 \) nm, the resistivity rapidly increases as the film becomes thinner. One possible explanation for the thickness dependence of the resistivity is degradation by air exposure (see supplementary materials (available online at stacks.iop.org/SUST/35/07LT01/mmedia)). As film thickness decreases, FeSe layer near the interface may deteriorate more immediately, which may affect \( T_c \). Thus, deposition of a protection layer on FeSe/STO 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 5–30 nm which exhibited superconductivity with \( T_c \) much higher than that of bulk FeSe under ambient pressure. The observed \( T_c \) in the grown 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, except for films thinner than 10 nm. This thickness dependence of \( T_c \) 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.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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. We also thank A Ichinose at CRIEPI for the cross-sectional TEM experiment.

References

[1] Hsu F C et al 2008 Proc. Natl Acad. Sci. 105 14262–4
[2] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2008 Appl. Phys. Lett. 93 152505
[3] Sun J P et al 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 180520
[5] Shi M Z et al 2018 New J. Phys. 20 123007
[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 077002
[7] Shigai J, Ito Y, Mitsuhashi T, Nojima T and Tsukazaki A 2016 Nat. Phys. 12 42
[8] Wang W K et al 2016 Chin. Phys. Lett. 33 057401
[9] Hanazawa K, Sato H, Hiramatsu H, Kamiya T and Hosono H 2016 Proc. Natl Acad. Sci. 113 3986–90
[10] Kouno S, Sato Y, Katayama Y, Ichinose A, Asami D, Nabeshima F, Imay M, Maeda A and Ueno K 2018 Sci. Rep. 8 14731
[11] Shikama N, Sakishita Y, Nabeshima F, Katayama Y, Ueno K and Maeda A 2020 Appl. Phys. Express 13 083006
[12] Shikama N, Sakishita Y, Nabeshima F and Maeda A 2021 Phys. Rev. B 104 094512
[13] Wang Q Y et al 2012 Chin. Phys. Lett. 29 037402
[14] He S et al 2013 Nat. Mater. 12 605
[15] Liu D et al 2012 Nat. Commun. 3 931
[16] Lee J J et al 2014 Nature 515 245–8
[17] Ginzburg V 1964 Phys. Lett. 13 101–2
[18] Allender D, Bray J and Bardeen J 1973 Phys. Rev. B 7 1020–9
[19] Pedersen A K, Ichinokura S, Tanaka T, Shimizu R, Hitosugi T and Hirahara T 2020 Phys. Rev. Lett. 124 227002
[20] Faeth B D, Yang S L, Kawasaki J K, Nelson J N, Mishra P, Parzyck C T, Li C, Schlom D G and Shen K M 2021 Phys. Rev. X 11 021054
[21] Feng Z et al 2018 Sci. Rep. 8 4039
[22] Nabeshima F, Kawai M, Ishikawa T, Shikama N and Maeda A 2018 Jpn. J. Appl. Phys. 57 120314
[23] Ghini M, Bristow M, Prentice J C A, Sutherland S, Sanna S, Haghhighirad A A and Coldea A I 2021 Phys. Rev. B 103 205139
[24] Nakajima M, Ohata Y and Tajima S 2021 Phys. Rev. Mater. 5 044801
[25] Wang Q, Zhang W, Zhang Z, Sun Y, Xing Y, Wang Y, Wang L, Ma X, Xue Q K and Wang J 2015 2D Mater. 2 044012
[26] Zhai W, Li M, Chang C Z, Jiang J, Wu L, Liu C, Moodera J S, Zhu Y and Chan M H W 2018 Sci. Adv. 4 eaao2682
[27] Connell J G, Isaac B J, Ekanyake G B, Strachan D R and Seo S A 2012 Appl. Phys. Lett. 101 251607
[28] McQueen T M et al 2009 Phys. Rev. B 79 014522
[29] Farrar L S, Bristow M, Haghhighirad A A, McCollam A, Bending S J and Coldea A I 2020 npj Quantum Mater. 5 29
[30] 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 024509
[31] 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 020503
[32] Zhang W et al 2014 Phys. Rev. B 89 060506