In-situ growth of superconducting SmO$_{1-x}$F$_x$FeAs thin films by pulsed laser deposition

Silvia Haindl$^{1,2}$, Kota Hanzawa$^3$, Hikaru Sato$^1$, Hidenori Hiramatsu$^{1,3}$ & Hideo Hosono$^{1,3}$

Oxypnictide thin film growth by pulsed laser deposition (PLD) is one of many insufficiently resolved issues in the research of iron-based superconductors. Here we report on the successful realization of superconducting SmO$_{1-x}$F$_x$FeAs oxypnictide thin film growth by in-situ PLD on CaF$_2$ (fluorite) substrates. CaF$_2$ acts as fluorine supplier by diffusion and thus enables superconducting oxypnictide thin film growth by PLD. Films are grown heteroepitaxially and characteristically have a broad resistive normal-to-superconducting transition. Best films have onset transition temperatures around 40 K.

The proposed in-situ PLD film growth offers an alternative and cheap route for the fabrication of iron oxypnictides. PLD becomes now an additional option for iron oxypnictide synthesis.

Discovery of high-temperature superconductivity in iron oxypnictides$^1$ that crystallize in the ZrCuSiAs-structure$^2$ (so-called 1111) led to surprises, provoked expectations, and keeps on exerting fascination. Their high critical temperatures up to $T_c \approx 55$ K and their high upper critical fields $\mu_0 H_c^2 > 50$ T create an attractive goal for synthesis, engineering and science of oxypnictide thin films, however, their growth has been a challenge ever since 2008$^3$. In contrast to the high-temperature superconductor YBa$_2$Cu$_3$O$_{7-\delta}$, where film growth by in-situ PLD succeeded promptly after its discovery in 1987$^4$, in-situ PLD of iron oxypnictides has been an unresolved issue and this fact severely impedes the development of iron oxypnictide thin film applications. The furthermore difficult and expensive high-pressure single crystal synthesis of oxypnictides strongly motivates the search for complementary, faster, more feasible and cheaper fabrication techniques$^5$.

The main challenge for an in-situ PLD growth of superconducting iron oxypnictides is, in first instance, to balance the loss of stoichiometric transfer of high vapor pressure (volatile) elements such as F that is essential for doping and, thus, inevitable for inducing superconductivity in the parent compound. In general, PLD is a powerful tool for growing thin films from a stoichiometric source (target)$^6$. However, it becomes arbitrarily complicated for volatile species. Off-stoichiometric transfer in PLD$^7$ is commonly defeated by an enrichment of the target with the volatile element or by deposition under reactive conditions. For achieving F-doping in the as-grown films we propose here another method where F-doping is obtained via diffusion from the substrate. This approach enables the first successful growth of superconducting iron oxypnictide thin films by in-situ PLD.

From ex-situ to in-situ PLD

The first film growth attempts of F-doped LaOFeAs by PLD in ultra-high vacuum (UHV) in 2008 succeeded in heteroepitaxy of LaOFeAs on oxide substrates$^8$. Unfortunately, the resulting films were undoped and non-superconducting as a result of the volatility of fluorine. Because of the lack of stoichiometric transfer PLD of oxypnictides is sharply constrained. Furthermore, oxypnictide phase formation from the vapor phase is always in contest with the formation of impurity phases such as pure iron, arsenic oxides, iron arsenides, and rare-earth oxides$^9$.

An approach based on room-temperature deposition of ROFeAs (R = La, Sm) and a subsequent ex-situ heat treatment of the as-grown films in an evacuated silica-glass tube, that contains an additional RO$_1-x$F$_x$FeAs pellet, resulted in superconducting films, however with less control over epitaxy$^{10,12}$. Epitaxial RO$_1-x$F$_x$FeAs thin films were finally grown by fine tuning the parameters of the heat treatment and due to a rather accidentally formed rare-earth oxyfluoride impurity layer that acts as a seed$^{11}$. The investigation of critical current densities and the

$^1$Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology, Mailbox R3-1, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, Japan. $^2$Physikalisches Institut, Universität Tübingen, 72076 Tübingen, Germany. $^3$Materials Research Center for Element Strategy, Tokyo Institute of Technology, Mailbox SE-6, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, Japan. Correspondence and requests for materials should be addressed to S. Haindl (email: silvia.haindl@uni-tuebingen.de) or H. Hiramatsu (email: h-hirama@lucid.msl.titech.ac.jp)
upper critical field anisotropy of an epitaxially grown LaO$_{1-x}$F$_x$FeAs thin film with a thickness of 100 nm can thus be viewed as an early milestone$^{14}$. Nevertheless, PLD is used for the creation of nucleation centers on the substrate but the two-step route clearly deviates from a typical PLD film growth and suffers from insufficient control of F-doping level$^{15}$.

In the last five years advances in the growth of oxypnictide thin films were made by means of molecular beam epitaxy (MBE) which should be able to master film growth with volatile elements$^{16-18}$. However, also in MBE F-doping has first been introduced via diffusion from a fluorine containing capping layer or from a fluorine containing substrate. Other thin film growth methods such as chemical vapor deposition have not yet found their breakthrough in producing F-doped oxypnictides$^{19}$.

For an advance in PLD of oxypnictide thin films and application-oriented research all above summarized experiences suggest a reactive all in-situ PLD process, i.e. under tunable fluorine gas supply. This reactive process can only be performed under severe safety regulations, because fluorine gas is highly toxic. In order to tackle the challenge of oxypnictide thin film growth by an all in-situ PLD process, we have re-investigated oxypnictide thin film growth on different substrates (and templates) and found, alternatively, a fluorine supplier in CaF$_2$ substrates. Our results are directive for future oxypnictide thin film growth efforts.

**Methods**

**Thin film deposition.** Thin film deposition was carried out in a UHV chamber (base pressure $5 \times 10^{-9}$ mbar) using a Spectra Physics Quantum Ray INDI pulsed Nd:YAG laser ($2\omega$) with a fixed laser repetition rate setting of 10 Hz and a wave-length of 532 nm. Measurements of the pulsed beam energy were performed in front of the entrance window of the UHV chamber before each deposition. Energies of 20–25 mJ used for film deposition result in energy densities on the target surface of approximately 0.9–1.7 $\text{J cm}^{-2}$.

Deposition was performed on different single crystalline oxide substrates, MgO(100) ($a = 4.21 \text{Å}$), LaAlO$_3$ (100) ($a = 3.79 \text{Å}$), and on single crystalline alkaline earth halide CaF$_2$ (100) ($a = 5.46 \text{Å}$). Furthermore, film growth on Fe and BaFe$_2$As$_2$ buffered MgO substrates was investigated since the excellent in-plane lattice parameter matching is expected to facilitate epitaxial film growth of the 1111 oxypnictide phase. In the following this excursion on buffer layers is only shortly summarized and our focus will be on the results obtained for F-doped SmOFeAs on CaF$_2$ (100) substrates.

Commercially available CaF$_2$ substrates ($10 \times 10 \times 0.5 \text{ mm}^3$) from Furuchi Chemical Corporation were heated within the vacuum chamber by a high power diode laser system to the deposition temperature and were kept 5 min at this temperature prior to deposition. No special pre-treatment of the substrates was undertaken. The substrate temperature inside the vacuum chamber was monitored by a pyrometer and by a thermocouple. Optimal deposition temperatures are around 860 °C. The target-substrate distance was set to 25–30 mm.

**Target preparation.** The polycrystalline SmO$_{0.9}$F$_{0.1}$FeAs target used in the experiments was synthesized by a two-step solid state reaction. All processes except heating were performed in an argon-filled glove box. First, the precursor materials SmAs, Fe$_2$As and FeAs were synthesized by mixing elements of Sm, Fe, and As. They were mixed in the chemical composition of Sm:Fe:As = 1:3:3 and heated at 900 °C for 12 h in an evacuated silica tube. The resultant SmFe$_2$As$_3$ powder was then mixed with dehydrated Sm$_2$O$_3$ powder, where 10% of Sm$_2$O$_3$ was replaced by a 1:1 mixture of SmF$_3$ and Sm metal for F substitution, following the chemical reaction of SmFe$_2$As$_3$ + 0.9 Sm$_2$O$_3$ + 0.1 SmF$_3$ + 0.1 Sm $\rightarrow$ 3 Sm(O$_{0.9}F_{0.1}$)FeAs. The mixture compound Sm(O$_{0.9}F_{0.1}$)FeAs was pressed and heated in an evacuated silica-tube at 1300 °C for 40 h to obtain a sintered pellet. Phase purity of the resulting PLD target was examined by X-ray diffraction, indicating a small amount of FeAs impurity.

**Thin film characterization.** Standard characterization of the grown thin films was carried out by X-ray diffraction on a Rigaku SmartLab and on a Bruker AXS D8 Advance diffractometer, both equipped with Cu K$\alpha$ radiation. High resolution X-ray diffractometry (XRD) and reflectivity (XRR) analysis were performed using a Ge 2-bounce monochromator for the incident beam (Rigaku SmartLab). Film thicknesses were determined from XRD radiation. High resolution X-ray diffractometry (XRD) and reflectivity (XRR) analysis were performed using a Ge 2-bounce monochromator for the incident beam (Rigaku SmartLab). Film thicknesses were determined from XRD diffraction on a Rigaku SmartLab and on a Bruker AXS D8 Advance diffractometer, both equipped with Cu K$\alpha$ radiation.

Optical measurements were carried out using a double beam spectrophotometer (Jasco V-570). Film thicknesses were determined from XRD diffraction on a Rigaku SmartLab and on a Bruker AXS D8 Advance diffractometer, both equipped with Cu K$\alpha$ radiation. High resolution X-ray diffractometry (XRD) and reflectivity (XRR) analysis were performed using a Ge 2-bounce monochromator for the incident beam (Rigaku SmartLab). Film thicknesses were determined from XRD diffraction on a Rigaku SmartLab and on a Bruker AXS D8 Advance diffractometer, both equipped with Cu K$\alpha$ radiation.

**Results**

**Film growth on stable oxide substrates.** Iron oxypnictide thin film growth on stable oxide substrates - as already reported in refs 8 and 9 - is characterized by impurity phase formation such as Fe$_2$As and Sm$_2$O$_3$ that strongly compete with the 1111 oxypnictide phase formation. In-situ PLD of iron oxypnictides is thus characterized by a constrained window of deposition parameters such as temperature, energy density on the target surface and target-substrate distance. The lack of superconductivity in the films is mainly attributed to the F-loss during deposition but a crucial O- and As-deficiency cannot be excluded.

Whereas oxypnictide films can be grown epitaxially on BaFe$_2$As$_2$/MgO templates, films on Fe/MgO always contained a larger fraction of impurity phases. These results contradict the conjecture made by Thersleff that Fe could be a generic seed layer for the epitaxial growth of Fe-based superconductors in general$^{22}$. For both templates the absence of a superconducting transition in SmO$_{1-x}$F$_x$FeAs deposited films can be again explained primarily due to F-losses. Results of the apparently undoped SmOFeAs film are shown in Fig. 1.
Film growth on CaF$_2$. The lack in stoichiometric transfer during PLD for the growth of F-doped iron pnictides can be balanced by the use of CaF$_2$ substrates that serve as a fluorine supplier during deposition by diffusion. With this working hypothesis superconducting SmO$_{1-x}$F$_x$FeAs thin films were fabricated on CaF$_2$(001) substrates at temperatures around 860 °C. CaF$_2$ substrates were used in PLD of iron-based superconducting films with the basic idea of tuning epitaxial strain$^{23}$, but never with the aim of F doping. In contrast, a possible chemical influence of CaF$_2$ substrates on the superconducting properties was primarily neglected$^3$. Only a few exceptional studies like ref. $^{24}$ reported a possible chemical reaction of the CaF$_2$ substrate even for iron chalcogenide thin films, where deposition temperatures are typically below 400 °C. Chemical reactions have to be considered at higher deposition temperatures used in our case and in the case of BaFe$_2$As$_2$ thin film growth.

In the following we demonstrate that thin film growth of superconducting iron oxypnictides is realized on CaF$_2$. No impurity phases except a small amount of Fe were detected by XRD (Fig. 2a). The best film has an onset transition temperature, $T_c$, near 40 K. The $c$-axis lattice parameters of the PLD grown films (8.63–8.66 Å) are comparable to the reported $c$-axis lattice parameters for MBE grown films (8.55–8.65 Å)$^{18}$ but generally larger than 8.495 Å ($x=0$), 8.428 Å ($x=0.1$)$^{25}$, or 8.488–8.498 Å ($x=0.2$)$^{26}$, in sintered polycrystalline powder samples and also larger than the $c$-axis in a single crystal (8.468 Å for $x=0.14$)$^5$.

Asymmetric Bragg reflections indicate the presence of diffusion layers or gradients. The lattice parameter change with film thickness can be estimated by a fit of the reflection intensity composed of a superposition of several peak profiles. The asymmetry intensifies with higher order, exemplarily the 008 reflection is shown (Fig. 2c). According to a simple fit the estimated relative change in the $c$-axis lattice parameter is slightly less than 1%.

Heteroepitaxial growth of SmO$_{1-x}$F$_x$FeAs on CaF$_2$ was confirmed by pole figure measurements (Fig. 2d,e) and is characterized by the following orientation relationship: (001)[100]SmO$_{1-x}$F$_x$FeAs||(001)[110]CaF$_2$. SmO$_{1-x}$F$_x$FeAs grows with the $c$-axis perpendicular to the substrate surface and its basal plane $a \times a$ is rotated by 45° in-plane versus the unit cell of CaF$_2$. 

---

**Figure 1.** (a) High resolution XRD (2θ/ω-scan) of SmOFeAs/BaFe$_2$As$_2$/MgO. 00$l$ reflections of each phase are indexed. The BaFe$_2$As$_2$ layer (Ba-122) has a thickness of about 16 nm ($c_{122}=12.97$ Å). The SmOFeAs layer (Sm-1111) was deposited at 860 °C and is about 36 nm thin ($c_{1111}=8.53$ Å). (b) No superconducting transition is detected in the electrical resistance measured down to 2 K.

**Figure 2.** (a) High resolution XRD (2θ/ω-scan) of SmO$_{1-x}$F$_x$FeAs/CaF$_2$. 00$l$ reflections of the 1111 phase and the substrate are indexed. The obtained lattice parameter is $c_{1111}=8.66$ Å. Small amount of Fe impurity is found as indicated by the Fe 110 reflection. (b) A total film thickness of 58.4 nm was evaluated from a fit of the normalized XRR intensity in the range of 2θ=0.6°–1.8°. (c) 008 Bragg reflection with total maximum at 2θ≈90.9° as a superposition of two extremal profiles $p_1$ (with maximum at 2θ≈90.9°) and $p_2$ (with maximum at 2θ≈92.1°). (d) Pole figure ($\psi$, $\phi$) for 2θ=47.0°±1.0° with CaF$_2$ 202 and SmO$_{1-x}$F$_x$FeAs 104 reflections. (e) Pole figure ($\psi$, $\phi$) for 2θ=30.0°±1.2° with CaF$_2$ 111 and SmO$_{1-x}$F$_x$FeAs 102 reflections.
Apart from droplets, i.e. particles of larger size typically observed on the surface of PLD grown films, the global surface topography is characterized by defects that evolve along the crystallographic [100] and [010] directions of the SmO₁₋ₓFₓFeAs film (Fig. 3a–d). These line-shaped defects appear in films grown on CaF₂ substrates and originate very likely from cracks. Such cracks are also observed to appear during scanning electron microscopy (SEM) where whole crack networks are induced under the scanning electron beam obviously by local heat generation in the CaF₂ substrate. SEM characterization of the films is thus a destructive procedure. Two consecutive scans demonstrate the appearance of defects within a short time (Fig. 3g,h). It is therefore plausible that the observed defect structure in the surface topography is caused by the bursting of the film surface. These defects increase the surface roughness (global rms ≈ 10 nm in a 10 × 10 μm² scan including droplets vs. local rms ≈ 1 nm in a 1 × 1 μm² scan), and also deteriorate the current flow (and critical currents) in the films leading most likely to current percolation.

The growth mode distinguishes from a layer-by-layer and resembles an island (Volmer-Weber) growth, where terrace-like structures with step sizes of approximately 1 and 2 unit cells can be identified (Fig. 3e,f). Because of low film growth rates (≤ 1 Å s⁻¹) deposition times of 5–10 min are required for film thicknesses of 20–50 nm. With increasing deposition time (>5 min) at elevated temperatures crack formation in the as-grown films is observed by AFM imaging that might be a result of outgassing fluorine leading to a bursting of the film layer along its crystallographic c-axis. CaF₂ substrates are not yet perfectly suitable for technological applications.

Electrical resistance of the films measured in van-der-Pauw geometry for applied magnetic fields parallel and perpendicular to the film c-axis (Fig. 4a). Qualitatively, the resistive transitions are very broad. The usually applied resistance criteria for 90%, 50%, and 10% of the normal resistance result in Tc,90 ≈ 35 K, Tc,50 ≈ 28 K, and Tc,10 ≈ 24 K. The broad transitions and the changes in the slope of R(T) within the normal–to-superconducting transition are characteristic for an inhomogeneous film due to F-doping gradients. Current percolation caused by the observed defects can have additional effects on broadening. The upper critical field (Fig. 4b) extracted from the 90% criterion has moderate slopes of dHc₂/dT ≈ −2.7 TK⁻¹ (−1.3 TK⁻¹) for μ0Hc₂[ab] (μ0Hc₂[ab]). The maximum slope of dHc₂/dT ≈ −5.5 TK⁻¹ estimated from the 90% criterion for μ0Hc₂[ab] corresponds to reported values in sintered powders²².

**Discussion and Conclusion**

The experiments have confirmed that superconductivity in iron oxyxnictides depends sensitively on the stoichiometry of the rare earth oxide layer in the 1111 unit-cell. O-deficiency turns out to be an additional drawback for the in-situ PLD process of oxyxnictides. Successful growth of superconducting iron oxyxnictides by PLD must, therefore, supply enough oxygen and fluorine during film growth. These results are in accordance with investigations of O-deficient oxyxnictides, RO₁₋ₓFeAs, that are not superconducting²¹. A precise stoichiometric control stays still a technological challenge for these materials and might be realizable only after optimization or in a reactive fabrication process. The essential supply of fluorine during film growth for doping and stabilizing the rare earth oxide layers is enabled by a diffusion process. This new solution deviates from the usual PLD philosophy.
that relies on the stoichiometric transfer of material from the target to the substrate. In using F-diffusion provoked by the substrate, latter becomes an additional source of material in the described in-situ PLD process.

The choice of brittle CaF$_2$ substrates is not yet optimal for applications of Fe-based superconductor thin films, a fact that has been widely neglected in the thin film growth of Fe-based superconductors in general. In future CaF$_2$ should be replaced by other materials that act as F-suppliers and, simultaneously, have better mechanical properties. As a remark: The observed enhancement in critical temperatures in Co-doped BaFe$_2$As$_2$ thin films grown on CaF$_2$ is very likely a result of a fluorine interdiffusion from the substrate to the film followed by a change in stoichiometry and lattice parameters. Similar defects (cracks) as described above appear in the surface morphology of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ films, too. Considering the difficult and rare synthesis of iron oxypnictide single crystals or thin films in general the importance of having a standard fabrication process for oxypnictides is evident. Our results indicate once more the requirement of a highly advanced process for machining iron oxypnictides into competitive superconducting applications. The above presented iron oxypnictide film fabrication route by in-situ PLD allows film growth and further development. With an in-situ PLD process for SmO$_{1−x}$Fe$_x$As the already developed concepts of coated conductor technology can be adapted as it was demonstrated by a first proof-of-concept for FeSe$_{1−x}$Te$_x$ and Co-doped BaFe$_2$As$_2$ superconductors already. Since film growth by MBE is still expensive and difficult to upscale towards an industrial level, a suitable PLD fabrication process represents a substantial step towards a reliable application-oriented research on iron-oxypnictides.

To summarize, the here reported successful in-situ growth of superconducting oxypnictide thin films by PLD on CaF$_2$ substrates represents a significant progress in the fabrication of F-doped oxypnictide thin films. In-situ PLD of superconducting iron oxypnictides seemed to be impossible due to a lack in stoichiometric transfer and the loss of fluorine as a dopant. Fluorine supply by diffusion from the CaF$_2$ substrate is, however, able to introduce sufficient doping. We have demonstrated that the use of the substrate as additional material source represents a methodological advance in PLD against material loss due to volatile components. Furthermore, the diffusion process offers at present a cheap solution to the problem of F-doping during film growth and circumvents chemical hazards of a fully reactive process.

References
1. Y. Kamihara, T. Watanabe, M. Hirano & H. Hosono. Iron-Based Layered Superconductor La[O$_{1−x}$F$_x$]FeAs (x = 0.05−0.12) with $T_c = 26$ K. J. Am. Chem. Soc. 130, 3296 (2008).
2. V. Johnson & W. Jeitschko. ZrCuSiAs: A ‘filled’ PbFCl type. J. Solid State Chem. 11, 161 (1974).
3. S. Haindl et al. Thin film growth of Fe-based superconductors: from fundamental properties to functional devices. A comparative review. Rep. Prog. Phys. 77, 046502 (2014).
4. D. Dijkkamp et al. Preparation of Y-Ba-Cu oxide superconductor thin films using pulsed laser evaporation from high $T_c$ bulk material. Appl. Phys. Lett. 51, 619 (1987).
5. N. D. Zhigadlo et al. Single crystals of superconducting SmFeAsO$_{1−x}$F$_x$ grown at high pressure. J. Phys.: Condens. Matter 20, 342202 (2008).
6. D. B. Chrisey, G. K. Hubler (eds). Pulsed Laser Deposition of Thin Films. Wiley, New York (1994).
7. J. Schou. Physical aspects of the pulsed laser deposition technique: The stoichiometric transfer of material from target to film. Appl. Surf. Sci. 255, 5191 (2009).
8. H. Hiramatsu, T. Katase, T. Kamiya, M. Hirano & H. Hosono. Heteroepitaxial growth and optoelectronic properties of layered iron oxyarsenide, LaFeAsO. Appl. Phys. Lett. 93, 162504 (2008).
9. H. Hiramatsu, T. Kamiya, M. Hirano & H. Hosono. Heteroepitaxial film growth of layered compounds with the ZrCuSiAs-type and ThCrSi$_2$-type structures: From Cu-based semiconductors to Fe-based superconductors. Physica C 469, 657 (2009).
10. E. Backen et al. Growth and anisotropy of La(O,F)FeAs thin films deposited by pulsed laser deposition. Supercond. Sci. Technol. 21, 122001 (2008).
11. S. Haindl et al. High Upper Critical Fields and Evidence of Weak-Link Behavior in Superconducting LaFeAsO$_{1−x}$F$_x$ Thin Films. Phys. Rev. Lett. 104, 077001 (2010).
12. M. Kidszun et al. Fabrication of superconducting oxypnictide thin films. EPL 90, 57005 (2010).
13. M. Kidszun et al. Epitaxial LaFeAsO$_{1−x}$F$_x$ thin films grown by pulsed laser deposition. Supercond. Sci. Technol. 23, 022002 (2010).
14. M. Kidszun et al. Critical Current Scaling and Anisotropy in Oxypnictide Superconductors. Phys. Rev. Lett. 106, 137001 (2011).
15. S. Haindl, M. Kidszun, F. Onken, A. Mietke & T. Thersleff. Lessons from Oxypnictide Thin Films. *Int. J. Mod. Phys. B* **27**, 133001 (2013).
16. T. Kawaguchi *et al.* *In situ* growth of superconducting NdFeAs(O,F) thin films by molecular beam epitaxy. *Appl. Phys. Lett.* **97**, 042509 (2010).
17. S. Ueda, S. Takeda, S. Takano, A. Yamamoto & M. Naito. High-$T_c$ and high-$J_c$ SmFeAs(O,F) films on fluoride substrates grown by molecular beam epitaxy. *Appl. Phys. Lett.* **99**, 232505 (2011).
18. H. Sugawara *et al.* One-step growth of SmFeAs(O,F) films by molecular beam epitaxy using FeF$_2$ as a fluorine source. *Supercond. Sci. Technol.* **28**, 015005 (2015).
19. I. Corrales-Mendoza, A. Conde-Gallardo & V. M. Sánchez-Reséndiz. Nd$_{1-x}$Fe$_x$OF Thin Films Deposited by Chemical Vapor Deposition and Their Arsenic Diffusion. *IEEE Trans. Appl. Supercond.* **21**, 2849 (2011).
20. I. Horcas, R. Fernández, J. M. Gómez-Rodriguez, J. Colchero, J. Gómez-Herrero & A. M. Baro. W$\times$M$\times$: A software for scanning probe microscopy and a tool for nanotechnology. *Rev. Sci. Instrum.* **78**, 013705 (2007).
21. Y. Muraba, S. Iimura, S. Matsuishi & H. Hosono. Hydrogen-Substituted Superconductors SmFeAsO$_{1-x}$H$_x$ Misidentified As Oxygen-Deficient SmFeAsO$_{1-x}$. *Inorg. Chem.* **54**, 11567 (2015).
22. T. Thersleff *et al.* Coherent interfacial bonding on the FeAs tetrahedron in Fe/Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ bilayers. *Appl. Phys. Lett.* **97**, 022506 (2010).
23. I. Tsukada *et al.* Epitaxial Growth of FeSe$_{0.5}$Te$_{0.5}$ Thin Films on CaF$_2$ Substrates with High Critical Current Density. *Appl. Phys. Express* **4**, 053101 (2011).
24. A. Ichinose *et al.* Microscopic analysis of the chemical reaction between Fe(Te,Se) thin films and underlying CaF$_2$. *Supercond. Sci. Technol.* **26**, 075002 (2013).
25. Z.-A. Ren *et al.* Superconductivity at 55 K in Iron-Based F-Doped Layered Quaternary Compound Sm[O$_{1-x}$F$_x$]FeAs. *Chin. Phys. Lett.* **25**, 2215 (2008).
26. C. Wang *et al.* Low-temperature synthesis of SmO$_{0.4}$F$_{0.6}$FeAs superconductor with $T_c$ = 56.1 K. *Supercond. Sci. Technol.* **23**, 055002 (2010).
27. W. Si *et al.* Iron-chalcogenide FeSe$_{0.5}$Te$_{0.5}$ coated superconducting tapes for high field applications. *Appl. Phys. Lett.* **98**, 262509 (2011).
28. T. Katase *et al.* Biaxially textured cobalt-doped BaFe$_2$As$_2$ films with high critical current density over 1 MA/cm$^2$ on MgO-buffered metal-tape flexible substrates. *Appl. Phys. Lett.* **98**, 242510 (2011).

**Acknowledgements**

The work at Tokyo Institute of Technology was supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) through Element Strategy Initiative to Form Core Research Center. All authors thank Dr. Takayoshi Katase for synthesizing the polycrystalline PLD target disks. S.H. and H.Hi. acknowledge financial support by German Research Foundation (DFG HA5934/5-1). H. Hi. was also supported by the Japan Society for the Promotion of Science (JSPS) Challenging Exploratory Research (Grant Number 26630305), the JSPS Grant-in-Aid for Scientific Research on Innovative Areas *Nano Informatics* (Grant Number 25106007), and Support for Tokyotech Advanced Research (STAR).

**Author Contributions**

S.H., H.Hi. and H.Ho. supervised the project, S.H. has designed the study and carried out the experiments with help of K.H., H.S. and H.Hi. All authors have analysed the results and reviewed the manuscript.

**Additional Information**

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Haindl, S. *et al.* *In situ* growth of superconducting SmO$_{1-x}$F$_x$FeAs thin films by pulsed laser deposition. *Sci. Rep.* **6**, 35797; doi: 10.1038/srep35797 (2016).

© The Author(s) 2016