TOPICAL REVIEW

Superconducting properties of iron chalcogenide thin films

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Abstract
Iron chalcogenides, binary FeSe, FeTe and ternary FeTe$_x$Se$_{1-x}$, FeTe$_x$S$_{1-x}$ and FeTe:O$_x$, are the simplest compounds amongst the recently discovered iron-based superconductors. Thin films of iron chalcogenides present many attractive features that are covered in this review, such as: (i) easy fabrication and epitaxial growth on common single-crystal substrates; (ii) strong enhancement of superconducting transition temperature with respect to the bulk parent compounds (in FeTe$_{0.5}$Se$_{0.5}$, zero-resistance transition temperature $T_{\text{c0}}^{\text{bulk}} = 13.5$ K, but $T_{\text{c0}}^{\text{film}} = 19$ K on LaAlO$_3$ substrate); (iii) high critical current density ($J_c \sim 0.5 \times 10^6$ A cm$^{-2}$ at 4.2 K and 0 T for FeTe$_{0.5}$Se$_{0.5}$ film deposited on CaF$_2$, and similar values on flexible metallic substrates (Hastelloy tapes buffered by ion-beam assisted deposition) with a weak dependence on magnetic field; (iv) high upper critical field ($\sim 50$ T for FeTe$_{0.5}$Se$_{0.5}$, $B_{c2}(0)$, with a low anisotropy, $\gamma \sim 2$). These highlights explain why thin films of iron chalcogenides have been widely studied in recent years and are considered as promising materials for applications requiring high magnetic fields (20–50 T) and low temperatures (2–10 K).

Keywords: iron-based superconductors, iron chalcogenides, thin films, superconductors, critical current, upper critical field

1. Introduction
Iron chalcogenides are defined as binary compounds of iron and a chalcogenide element (Ch) belonging to group VIA of the periodic table. Several compounds are formed from the common valence states of Fe and Ch: FeCh, Fe$_2$Ch$_3$, Fe$_3$Ch$_4$ and FeCh$_2$. In some cases Fe is not stoichiometric as in Fe$_{1-x}$S ($\alpha = 0.1–0.2$). Iron oxides (Fe$_2$O$_3$ and Fe$_3$O$_4$) and sulfides (mostly Fe$_3$S$_4$) are widely used in the industry and show several interesting properties, except superconductivity, so they are not discussed in this review. Thin films of binary 1:1 iron selenides and tellurides FeCh (Ch = Se, Te) were extensively studied since the early 1970s. Optical, magnetic and others physical properties were investigated [1–7], but resistivity has not been studied at temperatures below 100 K, and thus the occurrence of superconductivity was not recognized. This was probably due to the presence of iron that was historically considered detrimental for superconductivity. The first papers on superconducting properties of pure and doped 1:1 thin films appeared only after the discovery of superconductivity at 7 K in polycrystalline FeSe [8].

Superconducting iron chalcogenides with the 1:1 composition are called the ‘11 family’ of iron-based superconductors. Other families have more complex structures: ‘1111’, such as LaFeAsO$_{0.89}$F$_{0.11}$ [9] and derived compounds; ‘111’ like LiFe$_{1-x}$As [10], and ‘122’ like BaFe$_2$As$_2$ [11]. Even if their critical temperature ($T_c$) is low compared with those of the 1111 or 122 families, the compounds of 11 family are attractive for at least two reasons: (i) relatively safe synthesis, owing to the absence of the poisonous and volatile arsenic and (ii) potential applications, owing to the high upper critical field $B_{c2}(0)$ approaching 50 T and its low anisotropy ($\gamma \sim 2$) [12]. The quality of 11 thin films was greatly enhanced recently,
Table 1. Summary of deposition parameters of iron chalcogenide epitaxial films prepared by PLD on various single crystal substrates, including SrTiO$_3$ (STO), LaAlO$_3$ (LAO), LaSrAl oxide (LSAO), LaSrAlTa oxide (LSAT), LaSrGa oxide (LSGO) and yttria-stabilized zirconia (YSZ). KrF excimer laser ($\lambda = 248$ nm) was used unless noted otherwise.

| Material       | Substrate                  | Deposition $T$ ($^\circ$C) | Frequency (Hz) | Laser shots | Film thickness (nm) | Base pressure (Pa) | Laser energy | Substrate–substrate distance (cm) | Notes                  | Reference |
|----------------|-----------------------------|-----------------------------|----------------|-------------|---------------------|-------------------|--------------|----------------------------------|------------------------|-----------|
| FeTe$_{0.5}$Se$_{0.5}$ | MgO, STO                   | 200–600                    | 5–10           | 9000–54000  | 100–200             | $5 \times 10^{-4}$ | 200–350 mJ pulse$^{-1}$ | N/A                       | YAG laser | [32] |
| FeTe$_{0.5}$Se$_{0.5}$ | MgO, STO, LAO               | 400                         | 5              | N/A         | 80–100              | $1.33 \times 10^{-3}$ | 0.74–2 J cm$^{-2}$ | 4–7                       | N/A                    | [25] |
| FeTe$_{0.5}$Se$_{0.5}$ | STO, LAO                    | 300–450                     | N/A            | N/A         | N/A                 | N/A               | 3 J cm$^{-2}$          | N/A                       | N/A                    | [34] |
| FeTe$_{0.5}$Se$_{0.5}$ | MgO                        | 180–500                     | N/A            | N/A         | 400                 | N/A               | N/A                       | N/A                       | [35] |
| FeTe$_{0.5}$Se$_{0.5}$ | MgO, LAO, STO, LSAO, LSGO, YSZ, LSAT, Al$_2$O$_3$ | 300                         | 10             | N/A         | 50                  | $1.33 \times 10^{-3}$ | N/A                       | N/A                       | [36] |
| FeTe$_{0.5}$Se$_{0.5}$ | MgO, MgO, STO, YSZ, LSAT, LAO, LSGO, CaF$_2$, SrF$_2$, BaF$_2$ | 280                         | 10             | N/A         | 36–175              | $1.33 \times 10^{-3}$ | N/A                       | N/A                       | [37] |
| FeTe$_{0.5}$Se$_{0.5}$ | MgO, MgO, STO, STO, MgO, CaF$_2$ | 300                         | 10             | N/A         | 50                  | $1.33 \times 10^{-3}$ | N/A                       | N/A                       | [38] |
| FeTe$_{0.5}$Se$_{0.5}$ | MgO, MgO, STO, STO, MgO, CaF$_2$, SrF$_2$, BaF$_2$ | 250–600                     | 3, 10, 30      | 9000–45000  | 70–400              | $(1–2) \times 10^{-3}$ | 350 mJ pulse$^{-1}$ | 5                        | [15] |
| FeTe$_{0.5}$Se$_{0.5}$ | MgO, MgO, STO, SrF$_2$       | 300–650                     | 3–10           | N/A         | 17–90               | $5 \times 10^{-7}$  | 2 J cm$^{-2}$           | 5                        | [39] |
| FeTe$_{0.5}$Se$_{0.5}$ | MgO, MgO, STO, MgO, STO, MgO, SrF$_2$, MgO, LaAlO$_3$ | 550                         | 3              | N/A         | 1.2–600             | $5 \times 10^{-7}$  | 2 J cm$^{-2}$           | 5                        | [40] |
| FeTe$_{0.5}$Se$_{0.5}$ | MgO, MgO, STO, MgO, MgO, SrF$_2$, MgO, LaAlO$_3$, MgO, MgO, SrF$_2$, MgO, LaAlO$_3$ | 30–650                     | 3              | N/A         | 1.2–600             | $5 \times 10^{-7}$  | 2 J cm$^{-2}$           | 5                        | [41] |
| FeTe$_{0.5}$Se$_{0.5}$ | MgO, MgO, STO, MgO, MgO, SrF$_2$, MgO, LaAlO$_3$, MgO, MgO, SrF$_2$, MgO, LaAlO$_3$, MgO, MgO, SrF$_2$, MgO, LaAlO$_3$ | 550                         | 3              | N/A         | 1.2–600             | $5 \times 10^{-7}$  | 2 J cm$^{-2}$           | 5                        | [16] |
| FeTe$_{0.5}$Se$_{0.5}$ | Fe-buffered MgO             | 450                         | 3              | N/A         | 95                  | $10^{-8}$          | 3–5 J cm$^{-2}$         | N/A                      | Fe buffer thickness = 20 nm | [14] |
| FeSe$_x$       | MgO, MgO, STO, LAO           | 380                         | N/A            | N/A         | 50–200              | $1.33 \times 10^{-4}$ | N/A                       | N/A                       | FeSe$_x$ | [42] |
| FeSe$_x$       | MgO                        | 320 and 500                | N/A            | N/A         | 140                 | N/A               | N/A                       | N/A                       | FeSe$_x$ | [43] |
| FeSe$_x$       | MgO                        | 250–500                     | N/A            | N/A         | 100–600             | $5 \times 10^{-4}$  | N/A                       | N/A                       | FeSe$_x$ | [44] |
| FeSe$_x$       | STO, LAO                    | 620                         | 2              | N/A         | N/A                 | $3 \times 10^{-4}$  | XeCl laser (308 nm)     | N/A                       | FeSe$_x$ | [45] |
| FeSe$_x$       | MgO, Al$_2$O$_3$, STO, LAO  | 610                         | 48             | N/A         | 1500–1800           | $1.33 \times 10^{-3}$ | 1.15 J cm$^{-2}$        | N/A                       | XeCl laser (308 nm)     | [50] |
| FeSe$_x$       | MgO, STO, MgO, LAO          | 540                         | 4              | N/A         | 8                   | $2 \times 10^{-4}$  | 100 mJ mm$^{-2}$        | N/A                       | XeCl laser (308 nm)     | [47] |
| FeTe$_x$       | LaSrAlTa oxide, LaSrAl oxide | 300–450                     | 5              | N/A         | 100                 | $3 J cm^{-2}$      | N/A                       | 10$^{-4}$ Torr O$_2$    | FeTe$_x$ | [26] |
and high current densities, $J_c$, in magnetic field have been reported [12–16].

Excellent reviews on bulk iron chalcogenides have been published as dedicated papers [17] or as chapters in the extended overviews of all iron-based superconductors [18–23]. This paper is one of the few reviews entirely dedicated to iron chalcogenide thin films after the work of Li et al [24].

This contribution is an updated review of superconducting properties of 11 thin films, with a special emphasis on recent improvements in the critical temperature, upper critical field and critical current values. This review is divided into five parts. In the first part the synthesis parameters for films fabricated by pulsed laser deposition (PLD) and other techniques are summarized and their influence on the film crystallinity and morphology is reviewed. The second part is dedicated to the superconducting critical temperature and factors that determine its difference from $T_c$ of the parent bulk compounds. The third part concerns the critical fields and related magnetic parameters. The fourth part contains most of the updates to the previous review [24] and is dedicated to recent results on enhanced critical current density and global pinning force. The last part summarizes the state of the art and the open issues in research on iron chalcogenide thin films. The first four parts are divided in subsections dedicated to the compositions reported in literature: FeTe$_x$Se$_{1−x}$, FeTe$_x$S$_{1−x}$, FeSe$_x$, FeTe and FeTe:O$_x$. Data on the PLD synthesis parameters, critical temperatures, critical fields, critical currents and global pinning forces of all the films reviewed in this contribution are summarized in tables for convenience and easy comparison.

### 2. Synthesis, morphology and crystalline structure

Most iron chalcogenide thin films reported in literature are fabricated by PLD, ablating sintered targets with an yttrium aluminum garnet (YAG) laser (fourth harmonic, $\lambda = 266$ nm) [25] or a KrF excimer laser ($\lambda = 248$ nm).

Several research groups explored a wide range of experimental conditions to fabricate high-quality, superconducting epitaxial thin films by PLD, such as deposition temperature; laser frequency, energy and the number of shots; and the distance between substrate and target (table 1). Besides FeTe:O$_x$ films, which are prepared in oxygen atmosphere ($P_{O_2} \leq 10^{-4}$ Torr) [26], the ablation of targets is carried out in high vacuum ($10^{-4}$–$10^{-6}$ Pa). PLD targets are produced by conventional sintering. For FeTe$_x$Se$_{1−x}$, stoichiometric amounts of Fe, Te and Se powders are sealed into a quartz tube and reacted at 400 °C for about one day; then they are pressed into pellets with a diameter of about 13 mm and a thickness of about 7 mm, resealed, and sintered at 800 °C for about 7 days. The same procedure is followed for FeTe$_x$S$_{1−x}$, but the first reaction is carried out at 800 °C for 12 h and the second one at 600 °C, again for 12 h.

There is very limited mention of superconducting films grown by other common techniques, such as molecular beam epitaxy [27, 28], metalorganic chemical vapor deposition (MOCVD) [29] and sputtering [30]. Recently, very thick (thickness 100 μm) superconducting films of FeSe ($T_{c\text{meas}} = 8$ K) were successfully deposited by electrochemical route [31].

This section presents the morphology and crystalline structure of epitaxial iron chalcogenide films. All these films are superconductors; however their superconducting properties, as well as the transport and magnetic properties, are described in other sections of this review. It is worth noting that the preparation of 11 films is safer than the synthesis of 1111 or 122 films, thanks to the absence of poisonous elements, but it still presents some difficulties related to the volatility of chalcogenide elements, which hinders the stoichiometry control.

#### 2.1. FeTe$_x$S$_{1−x}$ films

Mele et al [32] reported on 100–200 nm thick films of FeTeS grown epitaxially on MgO and SrTiO$_3$ (STO) substrates with a cube-on-cube orientation (figure 1). Besides an earlier paper on FeTeS films from the same authors [33], there are no other reports on FeTeS thin films prepared with an excimer laser. Yoshida et al [25] deposited epitaxial films showing the same kind of crystalline orientation using a YAG laser. Independently from the preparation technique, an interfacial reaction layer is formed between the film and STO substrate (figure 2(a)), but is absent for films on MgO (figure 2(b)).

#### 2.2. FeTe$_x$Se$_{1−x}$ films

FeTe$_x$Se$_{1−x}$ with $x = 0.5$ presents the highest $T_c$ at the ambient pressure amongst all 11 compounds. Consequently, many groups prepared thin films of FeTe$_{0.5}$Se$_{0.5}$ before trying other compositions. High-quality epitaxial FeTe$_{0.5}$Se$_{0.5}$ films were obtained on several substrates. Figure 3 shows x-ray diffraction (XRD) patterns of one of the first high-quality FeTe$_{0.5}$Se$_{0.5}$ films deposited on STO by Si et al [34]. The $\theta$–$2\theta$ scan shows only 00L peaks and the $\Phi$ scan suggest a four-fold symmetry with in-plane alignment between the film and substrate. The epitaxial growth of the film is confirmed by the high-resolution transmission electron microscopy (HRTEM) cross-sectional image shown in figure 4. Huang et al [35] reported on FeTe$_{0.5}$Se$_{0.5}$ films grown on MgO at various temperatures. They found that epitaxy is improved at higher deposition temperatures and a four-fold symmetry with narrow peaks is achieved at the maximum deposition temperature of 500 °C.

Imai et al [36] systematically compared the properties of relatively thin (50 nm) FeTe$_{0.5}$Se$_{0.5}$ films grown on eight substrates and reported epitaxial growth on MgO, STO and LaAlO$_3$ (LAO) (figure 5). In a following report [37] they extended their research to non-oxide substrates like CaF$_2$, which resulted in the best superconducting properties (figure 6). SrF$_2$ and BaF$_2$ were found to be less effective than CaF$_2$ [38]. They state that the key to high-quality 11 thin films is the absence of interfacial reactions between the FeTeSe film and the substrate (figure 7). Mele et al [15] and Bellingeri et al [16, 39–41] confirmed that smooth, cube-on-cube epitaxial FeTe$_{0.5}$Se$_{0.5}$ films can be obtained on several substrates: MgO, LAO, STO, yttria-stabilized zirconia (YSZ), MgO, CaF$_2$ and LiF. Iida et al [14] reported for the first
time the effective use of Fe buffer on MgO substrate. The Fe buffer grew at 45° to the MgO substrate, whereas the FeTeSe film showed the cube-on-cube epitaxial relation (figure 8).

Speller et al [30] reported the first attempt to prepare FeTeSe films by molecular beam epitaxy (MBE) in a single-stage process on several substrates (MgO, STO, LaSrAlTa oxide (LSAT) and YSZ). In contrast to PLD samples, they found large compositional variations in some samples. Results of post-deposition annealing indicate that the ternary Fe(Se,Te) phase has a limited thermodynamic stability, transforming to Fe(Se, Te)2 even at low temperatures. Epitaxy was reported only on MgO and STO substrates (figure 9), with the presence of a-axis grains rotated by 30° about the surface normal.

2.3. FeSe_x films

Several reports on FeSe thin films appeared shortly after the discovery of superconductivity in the parent bulk compound. One of the first reports on epitaxial films was by Nie et al [42], who studied tensile strain induced by MgO, STO and LAO single-crystal substrates; c-axis growth with 00L peaks was obtained on all substrates.

Wang et al [43] deposited smooth tetragonal FeSe_{1-x} films on (001) MgO substrates by PLD. They studied the effect of low-temperature distortion on superconductivity and crystallinity. Films deposited at a low temperature of 320 °C were oriented along the c-axis. However, the (101) peaks were dominant in the films deposited at 600 °C.

Wu et al [44] presented an early report on the PLD of FeSe films on MgO. In XRD φ scans they observed two kinds of domains with four-fold symmetry. The a-axes of major and minor domains were rotated by 45° and 0°, respectively, relatively to the MgO substrate orientation (figure 10).

Han et al [45] prepared FeSe_x (x = 0.80, 0.84, 0.88 and 0.92) thin films on STO, LSAT and LAO substrates by PLD. All films exhibited a single phase and c-axis oriented epitaxial growth. Increasing the Ar pressure reduced the film crystallinity, and the films deposited under P > 10 Pa were amorphous.

Since 2010, most research groups use PLD for growing FeTeSe films, which have higher Tc values than FeSe films. However, several FeSe films were grown by alternative techniques. One of the first examples is given by Jourdan and ten Haaf [28], who prepared FeSe by MBE and achieved the best results on YAIO_3 substrates cut in the (110) direction. Films grew epitaxially as confirmed by XRD patterns, and φ scan demonstrates that in-plane (100) and (010) axes of the FeSe thin film were aligned parallel to the (1–10) and (001) axes of the YAIO_3 substrate (figure 11). Song et al [46] reported on MBE of stoichiometric and superconducting FeSe crystalline thin films on double-layer graphene that was formed on SiC(0001). It was shown by scanning tunneling microscopy (STM) that this new kind of substrate can yield strain-free FeSe films. Very recently, Demura et al [31] demonstrated the growth of 100 μm thick films on metallic tapes by electrochemical route. In their preliminary work, the composition ratio of Fe and Se was controlled by electric potential (figure 12) and pH value (figure 13).

2.4. FeTe films

Han et al [47] prepared epitaxial and superconducting FeTe films on LAO, LSAT, MgO and STO (figure 14). No other
Figure 2. TEM cross-sectional images of FeTeS thin films deposited at 400 °C (a) on SrTiO$_3$ (100) single-crystal substrates, showing a possible interfacial layer; (b) on MgO (100) single-crystal substrates. The insets show the corresponding selected area electron diffraction patterns. Reproduced with permission from [32]. ©2010 IOP Publishing.

reports were published so far on thin films of FeTe, which is not a superconductor in the bulk form.

2.5. FeTe$_x$:O$_x$ films

The only report on oxygen-enriched FeTe$_x$:O$_x$ films was published in 2010 by Si et al [26]. XRD patterns show 00L peaks from the film and STO substrate, indicating a good out-of-plane alignment of the film. The Φ scan of the (112) peak from the thin film and substrate contains four peaks spaced by 90°, revealing a fourfold symmetry (figure 15).

3. Superconducting critical temperature

The superconducting transition of iron chalcogenide thin films is strongly affected by several factors that are reviewed in this section: chemical substitutions, deviations from nominal stoichiometry, deposition temperature, laser frequency, number of laser pulses, film thickness, pressure and substrate quality. Strong differences (summarized in table 2) between the critical temperatures of the parent bulk compounds and films have been observed.

Figure 3. (a) XRD θ–2θ scan of an FeSe$_{0.5}$Te$_{0.5}$ thin film on a (100) STO substrate. (b) Φ scan of the (112) peak from the FeSe$_{0.5}$Te$_{0.5}$ film and (c) from the STO substrate. Reproduced with permission from [34]. ©2009 American Institute of Physics.

Figure 4. HRTEM image of an FeSe$_{0.5}$Te$_{0.5}$ thin film on a (100) STO substrate. Reproduced with permission from [34]. ©2009 American Institute of Physics.

3.1. Effect of chemical substitutions and deviations from stoichiometry

FeSe, the first discovered compound of the 11 family [8], has a zero-resistance transition temperature $T^0_c = 8$ K. From the early stages of research on polycrystalline materials it was made clear that substitution of Se by an isovalent element like Te enhances the superconducting transition temperature up to 16 K [38]. Later, it was found that doping at the Te site induces superconductivity in FeTe, which is not a superconductor in the bulk form [47]. The dependence of $T_c$ on chemical substitutions in FeTe and FeSe binary compounds and the role of stoichiometry are discussed in this section.
on STO and 5.37 K on MgO. Yoshida et al. found that films deposited at 400 °C deviated from stoichiometry and had average compositions of FeTe\(_{0.49}\)S\(_{0.13}\) and FeTe\(_{0.85}\)S\(_{0.12}\) on STO and MgO, respectively. Consequently the \(T_c\) values were lower in these films than the stoichiometric bulk material: 3.54 K on STO and 5.37 K on MgO. Yoshida et al. [25] described a similar deviation for films deposited with the YAG laser: Te and S contents were lower in the films than in the targets, and the average composition of all films was FeTe\(_{0.58}\)S\(_{0.12}\). Using a target enriched in Te and S (composition FeTe\(_{0.20}\)S\(_{0.45}\)) they obtained a Te-rich film (composition FeTe\(_{1.57}\)S\(_{0.15}\)) with \(T_c^0 = 6.6\) K, which is close to the bulk \(T_c^0\). These results reveal that the volatility of S may severely hinder the enhancement of \(T_c\) in this system. This is the reason why the study of FeTe\(_{1-x}\)S\(_{1-x}\) films was almost abandoned.

3.1.2. FeTe\(_{1-x}\)Se\(_{1-x}\) films. The phase diagram of FeTe\(_{1-x}\)Se\(_{1-x}\) [17] reveals that the tetragonal–orthorhombic structural transition observed in FeSe is suppressed with increasing Te concentration. The highest \(T_c\) appears in the tetragonal phase near \(x = 0.5\). With a further increase of Te content, the \(T_c\) decreases, the antiferromagnetic ordering accompanying the tetragonal–monoclinic distortion emerges, and the bulk superconductivity disappears (figure 17).

Wu et al. [44] reported a systematic study of Se doping effect in FeTe films. Their result shows that \(T_c^0\) increases with Te doping consistently with the phase diagram. However, it is not clear if the values reported refer to the nominal composition of the target or to the real composition of the film.

Screening of literature reveals contradictory results on the stoichiometry deviations in high-quality films prepared from a FeTe\(_{0.5}\)Se\(_{0.5}\) target. Si et al. [34] grew a 100 nm thick FeTe\(_{0.5}\)Se\(_{0.5}\) thin film on STO with \(T_c^{\text{nom}} = 14\) K. Bellingeri et al. [40] reported even higher \(T_c^{\text{nom}}\) (21 K) for a 200 nm thick FeTe\(_{0.5}\)Se\(_{0.5}\) film on LAO. Both authors state that there was no any deviation from the target stoichiometry. On the contrary, Mele et al. [15] reported that the compositions of films grown on typical oxide substrates heavily deviate from the nominal composition: FeTe\(_{0.08}\)Se\(_{0.92}\) on MgO, FeTe\(_{0.14}\)Se\(_{0.86}\) on STO and FeTe\(_{0.35}\)Se\(_{0.65}\) on LAO, all deposited at 450 °C. The deviations from stoichiometry explain the small values of \(T_c\) for these samples. Consistently, high-quality films were obtained on CaF\(_2\) at lower deposition temperatures, so that
deviations from stoichiometry were modest: FeTe$_{0.35}$Se$_{0.41}$ at 300 °C had $T_\mathrm{c}^0 = 13.65$ K (figure 18).

3.2. Effect of deposition temperature and number and frequency of laser pulses

The experimental parameters of PLD obviously affect the quality of the films and their superconducting properties. The majority of reports discuss the properties of the film obtained in the ‘best conditions’. Detailed discussions on the variation of film quality with experimental conditions were given only in the few cases reported here.

3.2.1. FeTe$_x$Se$_{1-x}$ and FeSe films. Wu et al [44] reported the thickness dependence of $T_\mathrm{c}$ for FeTe$_x$Se$_{1-x}$ thin films ($x = 0, 0.5$). They found that the superconductivity of both FeSe and FeSe$_{0.5}$Te$_{0.5}$ films shows a strong thickness dependence: $T_\mathrm{c}^0$ reaches 8 K (true zero-resistance state) for FeSe$_{0.5}$Te$_{0.5}$ films thicker than 100 nm. In contrast, for FeSe thin films no true zero-resistance state exists unless the film is thicker than 300 nm (figures 19 and 20).

Huang et al [35] analyzed the deposition temperature dependence of $T_\mathrm{c}$ in FeTe$_{0.5}$Se$_{0.5}$ samples deposited on MgO. Films deposited above 400 °C show semiconducting behavior, while those deposited at lower temperatures are metallic. The maximum value of $T_\mathrm{c}^0 = 10.75$ K is reached at 310 °C. Increasing the deposition temperature improves epitaxy, but degrades superconductivity and eventually produces semiconducting films (figure 21).

Bellingeri et al [40] reported that the $T_\mathrm{c}$ of FeTe$_{0.5}$Se$_{0.5}$ films deposited on LAO reaches a maximum of 21 K ($T_\mathrm{onset}$) at about 200 nm (figure 22).

Mele et al [15] systematically analyzed the dependence of $T_\mathrm{c}$ of FeTeSe/CaF$_2$ films on the experimental parameters, exploring a wide range of deposition temperatures (from 250 to 450 °C). They found that $T_\mathrm{c}^0$ increases with decreasing the deposition temperature, as shown in figure 23: $T_\mathrm{c}^0 = 13.65$ K for the sample deposited at 300 °C. Further improvements were obtained by lowering the deposition frequency from 30 to 3 Hz (figure 24). At 3 Hz, $T_\mathrm{c}^0 = 16.18$ K was higher than the bulk value.

3.3. Effect of lattice parameters and cell distortion

The anion height, i.e. the distance between the Fe layer and anion X (X = As, P, Se and Te), was suggested [17] as a universal parameter characterizing $T_\mathrm{c}$ values of all iron-based superconductors (figure 25). The maximum $T_\mathrm{c}$ is reached when anion height reaches 1.38 Å. Another proposed parameter [16, 48, 49] is the X–Fe–X angle $\alpha$ in Fe(X)$_4$.
tetrahedra: $T_c$ peaks when $\alpha$ approaches the ideal value of 109° 47' (figure 26).

According to these plots, iron chalcogenides possess too large values of anion height and too small values of $\alpha$, and this explains why their $T_c$ values are smaller than those of the other families of iron-based superconductors. If the anion height of 11 compounds is reduced and $\alpha$ is enlarged, $T_c$ should increase. This means the $c$-axis should be compressed, and the $a$-axis expanded according to the Poisson effect. A simple way to achieve this effect is the application of uniaxial pressure along the $c$-axis. However, as reported in table 2, the result is controversial: $T_c$ increases significantly with applied external pressure for FeSe$_x$ and FeTe$_{0.5}$Se$_{0.5}$ bulk samples, but unexpectedly decreases for FeTe$_{0.8}$S$_{0.2}$.

Focusing on thin films, the lattice mismatch between film and substrate allows to modify the crystal parameters, simulating the application of high external pressures. Lattice mismatch is defined as $M = 100(a_0 - a_s)/a_s$, where $a_s$ and $a_0$ are the lattice parameters of the substrate and bulk material, respectively. The crystal parameters of selected FeCh materials and typical substrates, together with the correspondent lattice mismatches, are summarized in table 3. From this table, the expected effects for 11 films grown on MgO, STO and CaF$_2$ are an expansion of $a$-axis and a compression of $c$-axis, with the concomitant $T_c$ enhancement. On the other hand, there is almost no mismatch on LAO, and thus the crystal parameters and $T_c$ should be almost unchanged.
Figure 12. XRD patterns of FeSe films electrodeposited at different electric potentials. Peaks marked by O, *, and ▲ indicate tetragonal FeSe, hexagonal FeSe, and hexagonal Se, respectively. Reproduced with permission from [31]. ©2012 Physical Society of Japan.

Figure 13. XRD patterns of FeSe thin films electrodeposited at several pH values. Peaks denoted by O and * indicate tetragonal FeSe and hexagonal FeSe, respectively. Reproduced with permission from [31]. ©2012 Physical Society of Japan.

The systematic analysis of literature reported in the following subsections shows that the situation is much more complex and the general prediction from the Poisson effect cannot be applied.

3.3.1. FeTe$_{1-x}$S$_{1-x}$ films. Yoshida et al [25] reported that the shrinkage of c-axis with respect to the bulk value increases $T_{\text{onset}}$ of PLD FeTe$_{1.57}$S$_{0.15}$ films prepared using a YAG laser. This result seems to confirm the general observation that the reduction of the anion height has a beneficial effect on the superconducting properties of 11 films (figure 27).

3.3.2. FeTe$_{1-x}$Se$_{1-x}$ films. Bellingeri et al [16, 39–41] extensively analyzed the properties of FeTe$_{0.5}$Se$_{0.5}$ films deposited on MgO, YSZ, STO, CaF$_2$, LiF and LAO. They reported a biaxial compressive strain effect by LAO substrate on 11 films, with shrinkage of both the a- and c-axes. Maximum $T_{\text{onset}}$ (21 K) was reported for the shortest a-axis of the film, while no dependence on the c-axis length was
Table 2. Summary of superconducting transition temperatures of polycrystalline (bulk) and thin films of iron chalcogenides. High-pressure data are reported for the bulk samples only. In the case of thin films, only the highest $T_c$ for each kind of compound is reported. EDS stands for energy dispersive X-ray spectroscopy.

| Nominal stoichiometry | Ambient pressure | High pressure | EDS composition | Ref. | Ambient pressure | High pressure | EDS composition | Substrate | Ref. |
|-----------------------|------------------|---------------|-----------------|------|------------------|---------------|-----------------|-----------|------|
| FeSe                  | 12               | 8             | 37 (4 GPa)      | N/A  | 12               | 8             | FeSe$_{0.91}$   | STO       | 50   |
| FeTe$_{0.5}$Se$_{0.5}$| 9                | 6.5           | 7 (1 GPa)       | FeTe$_{1.0}$Se$_{0.45}$ | 11            | 6.6           | FeTe$_{1.57}$Se$_{0.15}$ | STO | 25   |
| FeTe$_{0.5}$S$_{0.5}$  | 16               | 13.5          | 25 (2 GPa)      | N/A  | 21               | 19            | N/A             | LAO       | 16   |
| FeTe$_{0.5}$S$_{0.5}$  | 0                | 0             | N/A             | N/A  | 13               | 9             | N/A             | LAO       | 47   |

Figure 16. Phase diagram of FeTe$_{1-x}$S$_x$ superconductor. Reproduced with permission from [17]. ©2010 Physical Society of Japan.

Figure 17. Phase diagram of FeTe$_{1-x}$Se$_x$ superconductor. Reproduced with permission from [17]. ©2010 Physical Society of Japan.

observed. Indeed, the 21 K film has $\alpha \sim 10^4^\circ$, the closest to ideal one amongst the films prepared on LAO, as well as the shortest anion height (figure 28).

Figure 18. Temperature dependence of the normalized resistance of FeTeSe thin films deposited on STO, MgO, LAO and CaF$_2$ single-crystal substrates at 450 °C with 45000 laser pulses and 30Hz repetition frequency. The inset shows details of the superconducting transition. Reproduced with permission from [15]. ©2012 IOP Publishing.

Figure 19. The temperature dependence of the resistivity of FeSe$_{0.5}$Te$_{0.5}$ films. Zero resistance appears as film thickness increases to more than 100 nm. The inset shows the strong thickness dependence of onset $T_c$. Reproduced with permission from [44]. ©2009 Elsevier.

Mele et al [15] reported that FeTe$_{0.5}$Se$_{0.5}$ films deposited on LAO had a compressed c-axis ($c = 5.9293$ versus 5.9784 Å in the bulk), but their $T_c$ was lower than in the corresponding bulk material ($T_c^0 = 7.47$ versus 13.5 K in the bulk). They also
found that the c-axis of FeTe$_{0.5}$Se$_{0.5}$ films on MgO and STO were compressed ($c = 5.9228$ and $5.9116$ Å, respectively), as expected, although the films exhibited lower $T_c$ values. On the contrary, there is more clear correlation between $T_c$ and c-axis in the case of CaF$_2$: c-axis is unexpectedly longer than 6 Å, and $T_c$ is higher than in the bulk material. These results suggest the c-axis expansion and the resulting epitaxial strain along the a-axis play an important role in the $T_c$ increase on CaF$_2$.

Imai et al [36] showed that a thin FeTe$_{0.5}$Se$_{0.5}$ film (50 nm) deposited on CaF$_2$ at 300 °C had the most elongated c-axis (5.968 Å) and the largest $T_c^0$ (15.7 K). They claim that superconducting properties of the films are not affected by the a-axis and lattice mismatch, but by the ratio c/a and by the degree of the in-plane orientation. Speller et al [30] supported this idea and reported the $T_c$ dependence on the c/a ratio for their MBE samples and several films and bulk materials reported in literature. They suggest that that $T_c$ values are strongly affected by unit cell anisotropy, with an optimum c/a ratio of ~1.6 corresponding to the highest $T_c$ values of

Figure 22. In-plane lattice constant $a$ (a) and $T_c$ (b) values versus film thickness for FeSe$_{0.5}$Te$_{0.5}$ films on LAO, STO and YSZ substrates: $T_c$ reaches a maximum of 21 K for a thickness of ~200 nm that corresponds to a minimum of $a$. (c) Resistivity vs temperature for films on LAO (thickness 9, 18, 36, 72, 150, 200, 280 and 420 nm): the room-temperature resistivity monotonically decreases with thickness. Inset shows details of the superconducting transition for some films. Reproduced with permission from [40]. ©2010 American Institute of Physics.
Table 3. Crystalline parameters of commonly used substrates and bulk iron chalcogenides, and the lattice mismatch between them.

| Substrate  | Crystalline parameter $a$ or $a/\sqrt{2}$ (Å) | Lattice mismatch FeTe$_{0.5}$Se$_{0.5}$ (%) | FeTe$_{0.8}$S$_{0.2}$ (%) | FeSe (%) |
|------------|---------------------------------------------|------------------------------------------|--------------------------|-----------|
| MgO        | 4.212                                       | $-11.08$                                  | $-10.5$                  | $-11.9$   |
| SrTiO$_3$  | 3.904                                       | $-2.89$                                   | $-2.47$                  | $-3.56$   |
| LaAlO$_3$  | 3.788                                       | 0.087                                    | 0.57                     | $-0.61$   |
| CaF$_2$    | 3.868                                       | $-2.13$                                   | $-1.62$                  | $-2.84$   |

*For CaF$_2$, $a/\sqrt{2}$ is reported.*

Figure 25. (a) Anion height dependence of $T_c$ in the typical Fe-based superconductors. Solid and open symbols indicate the data obtained at ambient pressure and under high pressure, respectively. (b) Schematic of the anion height from the Fe layer. Reproduced with permission from [17]. ©2010 Physical Society of Japan.

14 K (figure 29). This is consistent with reports that $T_c$ is very sensitive to anion height above the Fe plane in Fe-based superconductors.

Huang et al [35] reported that $T_c$ of FeTe$_{0.5}$Se$_{0.5}$ films grown on MgO has a maximum for $c \sim 6$ Å. They suggested that rather than directly associated with the changes in $c$-axis, this variation of $T_c$ may be linked to changes in the iron coordinating Se/Te tetrahedra, like the distance $\Delta d_{Se/Te}$. They also observed that the tetrahedral bond angle $\alpha$ does not significantly affect $T_c$ of 11 films, while it is a crucial parameter for the other families of iron-based superconductors.

3.3.3. FeSe films. In the early report by Nie et al [42], 50 nm thick FeSe films deposited on LAO were relaxed because their crystal parameters had almost the same values as in the parent bulk compound; the films had $T_{c\text{onset}} = 8$ K, which is 4 K lower than in the bulk. Interestingly, strained films deposited on STO and MgO are not superconductors.

Later, Jung et al [50] reported the growth of epitaxial FeSe films on several substrates (STO, LAO, Al$_2$O$_3$ and MgO). Their best film (deposited on STO) exhibited almost
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Figure 28. (a) Transition temperatures of several FeSe$_{0.5}$Te$_{0.5}$ films on LAO, STO and YSZ substrates as a function of the in-plane cell parameter $a$. In (b) and (c), transition temperatures of films deposited on LAO are plotted as a function of the Fe–(Se,Te) bond length and of the (Se,Te)–Fe–(Se,Te) bond angle, respectively. The stars represent the corresponding bulk values. Dashed lines are guide to the eye. Reproduced with permission from [39]. ©2009 IOP Publishing.

Figure 29. Relationship between $c/a$ and onset $T_c$ values in films deposited by low-temperature MBE (stars) compared with data from thin films and bulk FeTe$_{0.8}$Se$_{0.2}$ samples reported in literature. Reproduced with permission from [30]. ©2011 IOP Publishing.

3.3.4. FeTe films. Han et al [47] reported that the onset of superconductivity of 13 K has been introduced by interfacial stress, more specifically by the tensile stress, into the tetragonal non-superconducting FeTe compound. Corresponding to the maximum value of $T_c$, the tetrahedral angle $\alpha$ assumes a value of 95.4° (figure 31).

4. Critical fields

Magnetic field/temperature phase diagrams of iron chalcogenide thin films reported in literature were plotted from magnetoresistance data obtained in a static field ($H = 0–14$ T), usually using a quantum design physical property measurement system (PPMS), or in a pulsed field ($H = 0–85$ T). In the first case, the values of upper critical fields $H_{c2}(0)$ in the direction parallel and perpendicular to the $c$-axis are usually evaluated using the Werthamer–Helfand–Hohenberg (WHH) model [51]:

$$H_{c2}(0) = \frac{-0.69T_c(H_{c2}/dT)_{T=0}}{T_c}. $$

In the second case, direct extrapolation of $H_{c2}(0)$ is possible. The values of coherence length $\xi$ ($0$) are calculated from the Ginzburg–Landau relationship:

$$\xi = \frac{\Phi_0}{2\pi H_{c2}(0)^{1/2}},$$

where $H_{c2}$ is the upper critical field in the direction parallel to the $c$-axis. Anisotropy parameter is defined as $\gamma = H_{c2}/H_{c1}^0$.

Table 4 summarizes $H_{c2}(0)$ and other magnetic properties of 11 films reported so far.

4.1. FeTe$_{1-x}$S$_{1-x}$ films

In the early report by Mele et al [32], an irreversibility field of $H_{irr} = 9$ T ($c$-axis) was observed at 1.94 and 3.75 K for FeTe$_{0.8}S_{0.2}$ films deposited on STO and MgO, respectively. Values of $H_{c2}(0)$ estimated with the WHH model from 90% of the normal state resistivity, were $H_{c2}(0) = 62.1$ T for the
Table 4. Upper critical fields and related magnetic properties of 11 thin films deposited on various substrates.

| Material            | Substrate | $T_c^0$ (K) | $H_{c2}^0$ (0) (T) | $H_{c2}^1$ (0) (T) | $dH_{c2}^1$ T (T/K) | $dH_{c2}^2$ T (T/K) | $\xi_0(0)$ (nm) | $\xi_{ab}(0)$ (nm) | $\gamma$ | Reference |
|---------------------|-----------|--------------|-------------------|-------------------|-------------------|-------------------|----------------|-------------------|--------|-----------|
| FeTe$_6$S$_2$O$_2$  | MgO       | 5.37         | 73.17             | 51.00             | 14.33             | 15.63             | 2.10           | 2.01              | 1.06   | [32]      |
| FeTe$_6$S$_2$O$_2$  | SrTiO$_3$ | 3.54         | 62.09             | N/A               | 14.06             | N/A               | N/A            | N/A               | N/A    | [32]      |
| FeTe$_6$S$_2$O$_2$  | MgO       | 12           | 72.5              | N/A               | N/A               | N/A               | N/A            | N/A               | N/A    | [44]      |
| FeTe$_6$S$_2$O$_2$  | SrTiO$_3$ | 14           | 100               | N/A               | N/A               | N/A               | N/A            | N/A               | N/A    | [34]      |
| FeTe$_6$S$_2$O$_2$  | CaF$_2$   | 15           | 150               | N/A               | N/A               | N/A               | N/A            | N/A               | N/A    | [37]      |
| FeTe$_6$Se$_{0.5}$O$_{0.5}$ | LAO | 17.7 | 10.3 | N/A | N/A | N/A | 2.10 | 1.06 | 1.06 | [12] |
| FeSe                | LAO       | 14           | 14/N/A            | N/A               | N/A               | N/A               | N/A            | N/A               | N/A    | [45]      |
| FeSe                | STO       | 50           | 50/N/A            | N/A               | N/A               | N/A               | N/A            | N/A               | N/A    | [50]      |
| FeSe                | YAlO$_3$  | 9.2          | 25.7              | N/A               | N/A               | N/A               | N/A            | N/A               | N/A    | [28]      |
| FeTe                | STO       | 13           | 123               | N/A               | N/A               | N/A               | N/A            | N/A               | N/A    | [47]      |
| FeTe : O$_3$        | STO       | 200          | 200/N/A           | N/A               | N/A               | N/A               | N/A            | N/A               | N/A    | [26]      |

Figure 31. (e) Lattice constants $c$ for 32 FeTe films deposited on four different substrates. (f) Zero-resistance transition temperature $T_c^0$ versus Fe–Te–Fe bond angle for four FeTe films indicated by arrows in (e). Inset schematically shows the definition of the angles 1 and 2, which are the Fe$_{1}$–Te–Fe$_{2}$ and Fe$_{1}$–Te–Fe$_{3}$; angles, respectively. Angle 2 is equivalent to the tetrahedral angle $\alpha$ mentioned elsewhere. Reproduced with permission from [47]. ©2010 American Physical Society.

Sample deposited on STO and 74.2 T for the sample deposited on MgO, and the respective $\xi_0(0)$ values were 2.3 and 2.1 nm. In the case of MgO substrate, $H_{c2}^0(0) = 80.7$ T, and $\xi_{ab}(0) = 2.01$ nm. These FeTeS films were almost isotropic, with $\gamma = 1.09$.

4.2. FeTe$_{x}$Se$_{1-x}$ films

Wu et al [44] have published one of the first reports on FeTeSe thin films. The upper critical field $H_{c2}(0)$ of FeTe$_{0.5}$Se$_{0.5}$ on MgO was estimated at 72.5 T, which was about four times larger than that of the undoped FeSe sample.

Si et al [34] reported chalcogenide thin films with enhanced superconducting properties with respect to the corresponding bulk materials. They measured magnetoresistance in the $H \parallel c$ configuration for three kinds of FeTe$_{0.5}$Se$_{0.5}$ samples: parent bulk, film deposited on STO with the same $T_c$ as in the bulk, and film with $T_c$ enhanced by the strain effect. $H_{c2}$ was consequently estimated from magnetoresistance curves applying the WHH model. Using $T_{onset}$ values, $H_{c2}(0)$ of all the samples was estimated at 100 T.

Tsukada et al [37] reported enhanced $H_{c2}(0) = 120$ T (evaluated using $T_{mid}$ and the WHH theory) for FeTe$_{0.5}$Se$_{0.5}$ thin films deposited on CaF$_2$ (figure 32).

Later, Tarantini et al [12] directly evaluated the upper critical fields of FeSe$_{0.5}$Te$_{0.5}$/LAO films in pulsed fields up to 85 T. They clarified that the shape of $H_{c2}(T)$ curves for $H \parallel ab$ in chalcogenide films is inconsistent with the conventional WHH theory: $H_{c2}(0)^∥$ was close to 53 T, i.e., about half of the values extrapolated from the WHH model; $H_{c2}(0)^⊥$ was slightly smaller so that the anisotropy parameter $\gamma$ was $\sim 1$. Furthermore, the upper critical field in the perpendicular configuration showed extraordinarily steep slopes of $dH_{c2}/dT = 250–500$ T K$^{-1}$ near $T_c$ (figure 33). This behavior was attributed to the almost complete suppression...
shows H and the red solid curves correspond to the QH for H 60 T pulsed magnet (circles) (solid and open symbols correspond to Figure 33. (a), (b) Hc2(T) curves for two strained FeSe1−xTe x thin films with similar Tc measured in a 45 T dc magnet (triangles) and in a 60 T pulsed magnet (circles) (solid and open symbols correspond to H∥ab and H∥c, respectively). The black solid curves show Hc2 fits, and the red solid curves correspond to the Q vector of the Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state. The blue dashed line in (b) shows Hc2(T) calculated without taking FFLO instability into account. Fitting parameters are α = 1.2 and η = 0.9 for H∥c and αe−1/2 = 7 for H∥ab. Here, Q is measured in the units of Q0 = 4πkB Tc/hνcβ/3. (c) Superconducting transitions in low fields (H∥ab) for a FeSe1−xTe x film and a magnification close to 90% of the normal-state resistivity. (d) For the same sample, the detailed superconducting transitions in low fields (H∥ab) for a FeSe1−xTe x film and a magnification close to 90% of the normal-state resistivity. (d) For the same sample, the detailed superconducting transitions in low fields (H∥ab) for a FeSe1−xTe x film and a magnification close to 90% of the normal-state resistivity. (d) For the same sample, the detailed superconducting transitions in low fields (H∥ab) for a FeSe1−xTe x film and a magnification close to 90% of the normal-state resistivity. (d) For the same sample, the detailed superconducting transitions in low fields (H∥ab) for a FeSe1−xTe x film and a magnification close to 90% of the normal-state resistivity.

they observed an almost linear dependence Hc2(T) were quite short: ξab = 1.5 nm and ξc < 0.12 nm.

Direct measurements in pulsed fields showed that the upper critical fields of 11 films can be pushed up to about 50 T by epitaxial strain and doping, overcoming typical values of parent bulk compounds that are of the order of 40 T [52–54]. The values of Hc2(0) calculated by the WHH formula range from 14 to 100 T or more, but are generally much larger than the observed Hc2(0), suggesting the predominance of the Pauli paramagnetic effect. In any case, Hc2(0) is quite high considering the moderately low Tc in this system. For example, Hc2(0) for FeSe1−xTe x is almost twice as high as for Nb3Sn, despite their same Tc = 18 K. These properties may be important for future applications of 11 compounds.

4.3. FeSe films

Han et al [45] used the half-rise of the R(T) curve at the superconducting transition to determine Tc for each field in FeSe thin films deposited on LAO. The upper critical field Hc2(0) can be estimated at 14 T according to the WHH model, as shown in the inset of figure 34. This value is close to that obtained from polycrystalline samples. Jung et al [50] prepared FeSe films with Tc onset = 12 K on several substrates and estimated their Hc2 at 50 T using the WHH model and the values of 0.9 Tc onset. Jourdan and ten Haaf evaluated the upper critical fields of FeSe films deposited by MBE on YAlO3 substrates [28] in the field range 0–8 T in both orientations: they observed an almost linear dependence Hc2(T), similarly as in polycrystalline bulk samples. From the WHH theory, Hc2(0) = 9.2 T and Hc2(0) = 25.7 T, so that γ ≈ 3.

4.4. FeTe films

Han et al [47] introduced the onset of superconductivity at 13 K into the tetragonal non-superconducting FeTe compound by tensile stress on STO substrates. The upper critical field
Table 5. Critical currents and pinning characteristics of FeTe$_{0.8}$Se$_{0.2}$ and FeTe$_{0.5}$Se$_{0.5}$ thin films deposited on various substrates. Values of $T^0_c$, self-field and in-field $J_c$ ($H \parallel c$ direction) and $F_p^{\text{max}}$ were found in the main text of the references or evaluated from the $J_c$–$H$ plots. Please check references: [26] did not use LAO or FeTe$_{0.5}$Se$_{0.5}$. Reference is [13] and second substrate is IBAD-buffered hastelloy, not STO.

| Material         | Substrate | $T^0_c$ (K) | $J_c$ (MA cm$^{-2}$) $H \parallel c$ | Type of pinning | $F_p^{\text{max}}$ (GN m$^{-3}$) | Reference |
|------------------|-----------|-------------|--------------------------------------|-----------------|----------------------------------|-----------|
| FeTe$_{0.8}$Se$_{0.2}$ | MgO       | 5.37        | 0.04 @ 2 K 0.006 @ 2 K               | N/A             | N/A                              | [32]      |
| FeTe$_{0.8}$Se$_{0.2}$ | SrTiO     | 3.54        | 0.0001 @ 2 K 0.000002 @ 2 K         | N/A             | N/A                              | [32]      |
| FeTe$_{0.5}$Se$_{0.5}$ | CaF$_2$   | 15.5        | 0.05 @ 12 K 0.03 @ 10 K             | N/A             | N/A                              | [37]      |
| FeTe$_{0.5}$Se$_{0.5}$ | LaAlO$_3$ | 15          | 0.4 @ 4.2 K 0.3 @ 4.2 K             | N/A             | 20 @ 4.2 K, 20 T                 | [13]      |
| FeTe$_{0.5}$Se$_{0.5}$ | SrTiO, IBAD-buffered hastelloy | 11 | 0.15 @ 4.2 K 0.1 @ 4.2 K | N/A | 8 @ 4.2 K, 20 T | [13] |
| FeTe$_{0.5}$Se$_{0.5}$ | Fe-buffered MgO | 17 | 0.5 @ 4.2 K 0.06 @ 4.2 K | N/A | Intrinsic (⊥ c-axis) | [14] |
| FeTe$_{0.5}$Se$_{0.5}$ | LaAlO$_3$ | 19          | 0.12 @ 4 K 0.1 @ 4 K                | N/A             | Intrinsic (⊥ c-axis)            | [57]      |
| FeTe$_{0.5}$Se$_{0.5}$ | CaF$_2$   | 16.18       | 0.41 @ 4.2 K 0.28 @ 4.2 K           | N/A             | c-axis correlated 22 @ 4.2 K, 9 T | [16]      |
| FeTe$_{0.5}$Se$_{0.5}$ | LaAlO$_3$ | 19          | 0.12 @ 4 K 0.1 @ 4 K                | N/A             | c-axis correlated N/A           | [17]      |
| FeTe$_{0.5}$Se$_{0.5}$ | SrTiO     | 15.1        | 0.4 @ 4 K 0.2 @ 4 K                 | N/A             | c-axis correlated N/A           | [17]      |

Figure 35. Influence of magnetic field on superconductivity for a 90 nm thick FeTe film on STO. Inset shows upper critical fields deduced from the midpoint transition temperatures with $H_{c2}(0)$ extrapolated as 123.0 T. Reproduced with permission from [47]. ©2010 American Physical Society.

$H_{c2}(0)$ was estimated by the WHH theory as 123 T, much higher than that of FeSe (figure 35).

4.5. FeTe : O$_x$ films

Si et al [26] reported that superconductivity ($T^0_c = 8$ K) can be induced in FeTe films deposited on STO by incorporation of oxygen into the Te site. By using the WHH model, $H_{c2}(0)$ was estimated to be $\sim 200$ T from the $T_c$ onset of magnetoresistance curves (0–9 T). The linear fitting for $H_{c2}(T)$ yielded $dH_{c2}/dT = -23$ T K$^{-1}$.

5. Critical currents and pinning forces

Fabrication of high-quality epitaxial films belonging to the 122 and 1111 families of iron-based superconductors was developed earlier than for films belonging to the 11 family. The initial difficulties related to the volatility of arsenic under the pulsed laser irradiation were overcome, and 1111 and 122 films were obtained with $J_c$ values higher than in single crystals of the same composition [55, 56]. Despite their simpler structure and easier synthesis route in comparison with films belonging to other families, the quality improvement of epitaxial 11 films took a little longer time, and reports on high-$J_c$ iron chalcogenides are still relatively few.

Table 5 summarizes $J_c$ and global pinning force ($F_p$) values for the 11 films reported so far. Most of reports concern $J_c$ of FeTe$_{0.5}$Se$_{0.5}$. No data are available on critical currents of FeSe or FeTe : O$_x$ thin films.

5.1. Critical currents

5.1.1. FeTe$_{x}$S$_{1-x}$ films. In an early paper by Mele et al [32] on optimized FeTeS films deposited on MgO and STO the self-field $J_c$ was reported as $4 \times 10^4$ A cm$^{-2}$ for the film deposited on MgO. It was even lower for films deposited on STO under the same conditions, due to the formation of reactive interface (see section 2.1). The low $J_c$ can be attributed to the low values of $T_c$ (in both cases the $T_c$ was lower than in the bulk material).

5.1.2. FeTe$_{x}$Se$_{1-x}$ films. A relatively high $J_c$ value was first achieved by Tsukada et al [37] for FeTe$_{0.5}$Se$_{0.5}$ thin films deposited on CaF$_2$. They reported a very slow suppression of $J_c$ above 10 T: at $T = 4.5$ K, $J_c$ (10 T) = $5.9 \times 10^4$ A cm$^{-2}$ and $J_c$ (14 T) = $4.2 \times 10^4$ A cm$^{-2}$ (figure 36). Si et al [13] reported the magnetic field dependence of $J_c$ for FeTe$_{0.5}$Se$_{0.5}$ thin films deposited on LAO and flexible metallic substrates buffered with ion-beam assisted deposition (IBAD) (figure 37). On LAO, $J_c$ (OT, 4 K) was $5 \times 10^5$ A cm$^{-2}$ and the field dependence was not pronounced. On IBAD-buffered
substrates, $J_c$ was $2 \times 10^5$ A cm$^{-2}$ at 4 K and 0 T with almost similar in-field behavior. Iida et al [14] studied the effect of Fe buffer between MgO single crystals and FeTe thin film. They reported $J_c (0 \text{T}, 4.2 \text{K}) = 0.5 \times 10^6$ A cm$^{-2}$. They found that for $H \parallel c$, $J_c$ values were quickly decreasing with increasing $H$, indicating less flux pinning in this direction, whereas the reduction of $J_c$ with $H$ was very small for $H \perp c$ below 16 K (figure 38). Eisterer et al [57] reported on critical current densities of four FeTe thin films of different thickness prepared on LAO under similar deposition conditions; $J_c$ at 4.5 K ($B \parallel c$) was $\sim 10^5$ A cm$^{-2}$. The same field dependence in all samples was observed at 10 and 15 K. More recently, Bellingeri et al [16] reported $J_c$ plots for FeTeSe films deposited on STO and LAO. The critical current density of two films behaved very differently: the film on LaAlO$_3$ had higher $J_c$ for the field parallel than perpendicular to the $ab$ planes, while the opposite held for the SrTiO$_3$ sample. The $J_c$ values of the SrTiO$_3$ sample, at liquid He temperatures, stayed above $10^5$ A cm$^{-2}$ in the entire field range (figure 39). Similar results were reported by Mele et al [15] for FeTeSe films grown on CaF$_2$: the $J_c$ in zero field was $0.43 \times 10^6$ A cm$^{-2}$ at $T = 2$ K and remained above $0.26 \times 10^6$ A cm$^{-2}$ at 9 T (figure 40). Notably, the decrease of $J_c$ did not accelerate much in high fields at 4.2 K ($J_c = 0.41 \times 10^6$ A cm$^{-2}$ at 0 T and $0.23 \times 10^6$ A cm$^{-2}$ at 9 T). Recently, Higashikawa et al [58] reported a study of $J_c$ in FeTeSe thin films deposited on CaF$_2$ by means of scanning Hall probe microscopy. From the 2D-plane distribution of the current (figure 41), they estimated $J_c$ at 4.2 K as $\sim 1$ MA cm$^{-2}$, three times higher than the value directly measured by the four-probe method (figure 42). This fact suggests that FeTeSe thin films have a great potential for practical applications at low temperatures. Independently from the substrate, the common feature of all reports on FeTe thin films is a weak dependence of $J_c$ on magnetic field at liquid helium temperatures. This property is beneficial for high-field magnet applications.

Angular dependences of $J_c$ were reported for several of the FeTeSe films described above. In the FeTeSe/Fe/MgO films of Iida et al [14] the angular-dependent critical current densities ($J_c (H)$) at 8 K in several magnetic fields (figure 43) always showed a peak at $\theta = 90^\circ$ and $270^\circ$ ($H \perp c$) owing to the intrinsic pinning. There is no evidence of $c$-axis
Figure 39. $J_c$ versus magnetic field for samples deposited on LaAlO$_3$ (left panel) and on SrTiO$_3$ (right panel) for different temperatures (4 and 6 K for LaAlO$_3$ and 4 and 8 K for SrTiO$_3$—this means nearly the same $T = T_c$) and with $H$ perpendicular (solid symbols) and parallel (open symbols) to the $ab$ planes. Reproduced with permission from [16]. ©2012 IOP Publishing.

Figure 40. Magnetic field dependence of critical current density at $T = 2, 4.2$ and 10 K, in the field direction $B \parallel c$, for FeTeSe thin films fabricated by PLD at 300 °C and 3 Hz on single-crystal CaF$_2$ substrates. Reproduced with permission from [15]. ©2012 IOP Publishing.

Figure 41. Critical current distribution measured with a Hall probe on a 1 cm $\times$ 0.2 cm $\times$ 200 nm FeTe$_{0.5}$Se$_{0.5}$ thin film fabricated by PLD on CaF$_2$. Reproduced with permission from [58].

correlated pinning (peak for $H \parallel c$). Bellingeri et al [16] and Mele et al [15] reported a completely different behavior for FeTe$_{0.5}$Se$_{0.5}$ thin films deposited on STO, LAO and CaF$_2$. On LAO, $J_c$ monotonically increased with increasing angle, with no indication of $c$-axis-correlated defects. $J_c$ was independent of the field orientation up to 50° and the peak for $H \parallel ab$ was quite sharp: this is consistent with correlated pinning centers parallel to the film. In the case of the film deposited on SrTiO$_3$, pronounced anisotropy and a large peak at $\theta = 0°$ ($c$-axis peak) was observed at all temperatures and magnetic fields, indicating the presence of a strong pinning mechanism (figure 44). Similar behavior was observed on CaF$_2$ [15], although the $c$-axis correlated peak was very broad and appeared at $B \geq 3$ T (figure 45). The effect on STO and CaF$_2$ resembles the one observed in 122 films [56] and in YBa$_2$Cu$_3$O$_{7-\delta}$ films with embedded nanocolumns [59]. Furthermore, the presence of nanorods parallel to $c$-axis of the film was confirmed by Bellingeri et al [16] using surface STM, but not by Mele et al [15] who employed cross-sectional TEM. In the paper by Eisterer et al [57], the angular dependence of $J_c$ shows only the intrinsic peak ($B \perp c$) except for one sample that at 15 K shows the $B \parallel c$ peak.

Figure 42. Critical current versus temperature ($B = 0$ T) for 200 nm thick FeTe$_{0.5}$Se$_{0.5}$ thin film fabricated by PLD on CaF$_2$. $J_c$ evaluated by transport measurements (PPMS) is compared with $J_c$ calculated from Hall probe maps with two different electric field criteria ($E_c$). Reproduced with permission from [58].

Figure 43. Angular dependence of critical current density $J_c(\theta)$ of FeSe$_{1-x}$Te$_x$ film measured in several magnetic fields at 8 K. Reproduced with permission from [14]. ©2011 American Institute of Physics.
In summary, the reports on angular dependence of $J_c$ are contradictory and further investigations are required to clarify whether $c$-axis correlated pinning may be induced by the substrate.

5.2. Global pinning force

5.2.1. $FeTe_xSe_1-x$ films. Calculation of global pinning force $F_p = J_c \times B$ in the range 0–30 T reported in figure 46 shows that $F_p^{\text{max}}$ is about 20 GN m$^{-3}$ at 4.2 K for films deposited on LAO [13]. Films deposited on CaF$_2$ show a similar trend up to 9 T, the maximum magnetic field available for measurements by Mele et al [15]. Furthermore, Si et al [13] reported (figure 46) an interesting comparison at 4.2 K between FeTeSe/STO films, YBaCu oxide (YBCO)-coated conductors and metallic superconducting wires. FeTeSe performed better than metallic superconductors in high fields, whereas YBCO was superior in the entire ranges of field and temperature. However, it must be kept in mind that YBCO has problems with grain boundaries and anisotropy that seems to be absent in FeTeSe films (see previous sections and other chapters of this special issue). The analysis of pinning force by the Kramer’s law (continuous lines in figure 46) reveals that the FeTeSe system can be explained invoking pinning by point-like defects. Since the coherence length of FeTeSe is short (1–2 nm), improvements in $J_c$ and $F_p$ are expected by controlled introduction of engineered defects at the nanoscale, as in ceramic (YBCO) and 122 iron-based superconductors.

6. Conclusions

In July 2008, the discovery of superconductivity in polycrystalline FeSe generated much interest in the scientific community, with numerous papers published in the same year on bulk materials and single crystals. At the beginning, the main purpose was to clarify the mechanism of superconductivity in presence of a ferromagnetic element. Furthermore, the early evidence that the upper critical field of FeSe and related iron-chalcogenide compounds is quite large for their low $T_c$ favored them for practical applications. Consequently, since 2009 many research groups were attracted to the fabrication and characterization of iron-chalcogenide thin films. To date, several high-quality films with excellent transport properties in magnetic field have been produced and tested.

A variety of attractive features of iron-chalcogenide thin films was described in this review and can be summarized as
1. Epitaxial growth on common substrates. In comparison with compounds belonging to other families of iron-based superconductors, thin films of iron chalcogenides are relatively easy to grow by PLD. Cube-on-cube orientation and epitaxial growth are obtained on common single-crystal substrates (MgO, STO, LAO, CaF$_2$ and so on) under mild vacuum conditions ($\sim 10^{-4}$ Pa) and at moderate deposition temperatures (300–500 °C).

2. Enhancement of $T_c$ with respect to parent bulk compounds. Except for thin films of FeSe, which exhibits almost the same $T^0_c \sim 8$ K in the bulk and films, iron chalcogenide thin films have higher maximum $T_c$ values than their parent bulk compounds. FeTe$_x$S$_{1-x}$ shows $T^0_c = 6.6$ versus 6.5 K in the bulk; FeTe$_x$Se$_{1-x}$ films have $T^0_c = 18$ K on LAO and 16.15 K on CaF$_2$ ($T^0_c \sim 14$ K in the bulk); FeSe films have $T^0_c \sim 6$ K versus 4 K in the bulk; and, remarkably, FeTe : O$_x$ films have $T^c = 9$ K on LAO substrates, and FeTe : O$_x$ films have $T^c = 8$ K on STO, while the parent bulk compound are not superconductors.

3. High and almost isotropic upper critical field. Direct evaluation in pulsed fields reveals that the upper critical field at 0 K is about 50 T in the case of FeTe$_{0.5}$Se$_{0.5}$, which is quite high for compounds with relatively small $T_c$. Consequently, iron chalcogenide films may find applications requiring high fields (20–50 T) and low temperatures (2–10 K).

4. High critical currents with low magnetic field dependence. In the recent papers, impressive values of 0.5–0.6 MA cm$^{-2}$ at 4.2 K, 0 T have been reported for the critical current density of FeTe$_{0.5}$Se$_{0.5}$. Furthermore, the dependence of $J_c$ on magnetic field at liquid helium temperatures is weak, and this represents another advantage for in-field applications. Coherence length is on the order of few nanometers, and thus the in-field critical current can be enhanced by introduction of nanosized artificial pinning centers, as in the case of YBCO films.

5. Feasibility of thin films deposited on buffered metallic substrates. The feasibility of Fe buffers on single crystals for deposition of iron chalcogenide thin films has been demonstrated. Besides that, epitaxial films have been prepared on technical metallic substrates buffered with IBAD, without significantly reducing the critical current and upper critical field with respect to the films prepared on bare single crystals. A further progress in this direction will open the door for practical applications, similarly to what is happening now with the second generation of YBCO-coated conductors.

On the other hand, several issues remain open and are expected to be solved in the near future:

1. Control of stoichiometry. Chalcogenide elements (especially S and Se) are volatile and easily evaporate during the preparation of PLD targets. Evaporation may occur also in the PLD chamber during the fabrication of the films. The result is that the content of chalcogenides in the films is below the stoichiometric value, and therefore $T_c$ may be lower than expected. Targets with stoichiometric excess of chalcogenides, and/or in-plume PLD might help obtaining films with the desired stoichiometry.

2. Factors that enhance $T_c$ in films compared to bulk materials. It is believed that the enhancement of $T_c$ in iron chalcogenide films with respect to the parent bulk compounds is related to strain induced by the substrate. However, the experimental behavior of the films deviates from simple Poisson effect, and it is not possible to predict the change in $T_c$ from the lattice mismatch. To solve this puzzling issue, a systematic analysis of the variation of lattice mismatch, composition and thickness with experimental conditions is required for all types of iron chalcogenide films.

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