

In situ x-ray absorption and photoelectron spectroscopy on epitaxial Fe_xTe thin films with a wide range of Fe/Te compositions

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Fe_xTe thin films were prepared on SrTiO_3 (001) substrates by molecular beam epitaxy in a well-ordered epitaxial layer-by-layer fashion. The composition of the films was varied by adjusting the Te flux in a Te-limited growth regime. Changes in the electronic structure were systematically studied using *in situ* x-ray absorption spectroscopy at the Fe $L_{2,3}$ and Te $M_{4,5}$ edges and x-ray photoelectron spectroscopy of core levels and valence band. We found that FeTe with optimized composition (Fe/Te ratio ≈ 1) provides the sharpest spectral features, indicating that $\text{Fe}_{1.00}\text{Te}$ can be synthesized as a thin film, although it is not possible in bulk.

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I. INTRODUCTION

Since the first report of iron-based superconductivity [1], numerous studies have been conducted to understand the intriguing coexistence of magnetism and superconductivity in this class of materials [2–4]. The crystal structures of all iron-based superconductors share a common basic building block, a layer in which four pnictides or chalcogens tetrahedrally coordinate the iron atom and which is reported to provide the conduction electrons. Binary iron chalcogenides have the simplest structure, the tetragonal PbO -type structure, consisting of a stack of only these tetrahedral layers interconnected by van der Waals forces. Among them, iron selenide (FeSe) and iron telluride (FeTe) are the most studied compounds. Despite their apparent similarities, they exhibit surprising differences in electronic and magnetic behavior. FeSe is a superconductor in its near-stoichiometric form and shows no detectable long-range magnetic order for all temperatures [5–7]. FeTe , on the other hand, does not undergo a superconducting transition and has an antiferromagnetic low-temperature phase [8–10]. The origin of the divergent characteristics is still under debate. The influence of the larger size of the tellurium ion, structural differences with variations in bond lengths and angles, and changes in spin ordering or hybridization between Fe $3d$ and ligand p states have been discussed [11–13]. Furthermore, the seemingly unavoidable presence of excess iron in bulk FeTe has been proposed as a primary factor for the absence of superconductivity [10,14–20]. In contrast to the tetragonal phase of FeSe , which has a very narrow homogeneity range around the equiatomic, stoichiometric composition, bulk FeTe

with the same structure forms only in the presence of excess iron [21,22], namely, for Fe_{1+y}Te with $0.04 < y < 0.17$ [20].

The synthesis of FeTe samples with a reduced amount of excess iron is therefore of great interest for a better understanding of the superconductivity in this class of materials. Recently, it has been shown that a wider range of Fe/Te compositions can be achieved by growing FeTe in thin-film form, offering the prospect of getting closer to the stoichiometric, possibly superconducting compound $\text{Fe}_{1.0}\text{Te}$ [23]. Fe_xTe thin films were prepared by pulsed laser deposition (PLD) [24–28] and molecular beam epitaxy (MBE) [23,29–33] on various substrates. The reported properties vary widely due to a poor control of the composition and high susceptibility to oxidation. The incorporation of oxygen has been shown to change the valence state of the constituents and the resistivity behavior with the eventual emergence of a superconducting phase at low temperatures [25–29,32]. In fact, superconductivity has been also observed in Fe_xTe films after exposure to air [26,27,32], which further complicates the research. Careful sample preparation and special precautions during the measurements are of utmost importance for the investigation of the intrinsic character of FeTe .

In this work, we use molecular beam epitaxy under ultrahigh vacuum conditions to prepare Fe_xTe thin films on SrTiO_3 (001) substrates. The crystalline growth is investigated by *in situ* reflection high-energy electron diffraction and low-energy electron diffraction. By varying the tellurium flux under Te-limited growth conditions, we control the composition of the Fe_xTe films. The stoichiometry is carefully analyzed by spectroscopy using a bulk crystal with known composition as reference. All *in situ*, we systematically study the influence of the composition on the electronic structure using x-ray absorption spectroscopy at the Fe $L_{2,3}$ and Te $M_{4,5}$ edges, as well as core-level and valence-band photoelectron spectroscopy, thereby providing an extensive set of reliable reference spectra.

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II. EXPERIMENTAL DETAILS

The Fe_xTe thin films were grown by molecular beam epitaxy (MBE). The base pressure of the growth chamber was approximately 3×10^{-10} mbar. Epipolished SrTiO_3 (001) substrates were cleaned in acetone and isopropanol, followed by an *in situ* annealing at 600°C in an oxygen pressure of 3×10^{-7} mbar for 2 h to obtain clean, well-ordered surfaces. High-purity Fe and Te were evaporated from standard effusion cells. Before deposition, the relative flux rates of the materials were measured using a quartz crystal monitor at the growth position. The deposition time was fixed at 30 min.

In situ and real-time monitoring of the film growth was performed by reflection high-energy electron diffraction (RHEED) at 20 keV using a STAIB Instruments RH35 system. The incident electron beam was aligned parallel to the [100] crystallographic direction of the SrTiO_3 (001) substrates. The in-plane structural order was verified after growth by *in situ* low-energy electron diffraction (LEED). The images presented were taken at 65 eV electron kinetic energy.

The x-ray absorption (XAS) and x-ray photoelectron spectroscopy (XPS) measurements were performed *in situ* at the NSRRC-MPI TPS 45A submicron soft x-ray spectroscopy beam line in Taiwan, with a pressure of about 1×10^{-10} mbar in the measurement chamber.

The XAS spectra were collected at 80 K using the total electron yield (TEY) method. Reference Fe_2O_3 and Cr_2O_3 crystals were measured simultaneously in a separate chamber with the same photon beam to obtain relative energy referencing for the Fe $L_{2,3}$ and Te $M_{4,5}$ spectra. The photon energy of all XAS data was calibrated such that the first peak of the Fe L_3 of Fe_2O_3 is at 707.5 eV or the Cr L_3 of Cr_2O_3 at 575.92 eV.

An $\text{Fe}_{1.13}\text{Te}$ bulk single crystal was used as reference for the determination of the Fe/Te composition of the films. A clean surface was obtained by cleaving under ultrahigh vacuum conditions with a pressure lower than 2×10^{-10} mbar, followed by *in situ* transfer to the measurement chamber.

The XPS data were collected at 1000-eV photon energy in normal emission geometry and at 80 K using an MBS A-1 analyzer. The spot size on the samples was about $20 \times 60 \mu\text{m}^2$ for the films and $20 \times 40 \mu\text{m}^2$ for the bulk crystal. The Fermi level and the energy resolution were determined by measuring the metallic Fermi edge of a polycrystalline gold film. The total energy resolution was approximately 0.1 eV. All spectra were normalized by the incident light intensity.

X-ray diffraction (XRD) measurements were performed at the NSRRC-TPS 09A beam line at a photon energy of 12 keV ($\lambda = 1.0332 \text{ \AA}$). To prevent degradation during the *ex situ* characterization, the Fe_xTe films were capped with 12-nm tellurium layers [34] after the surface-sensitive spectroscopic measurements and before taking them out of the ultrahigh vacuum system.

III. RESULTS AND DISCUSSION

A. Crystalline growth and composition

Fe_xTe thin films were deposited on freshly annealed SrTiO_3 (001) at the substrate temperatures of 230°C , 250°C , and 300°C . The evaporation rates of iron and tellurium were fixed at 1 $\text{\AA}/\text{min}$ and 4 $\text{\AA}/\text{min}$, respectively. The electron

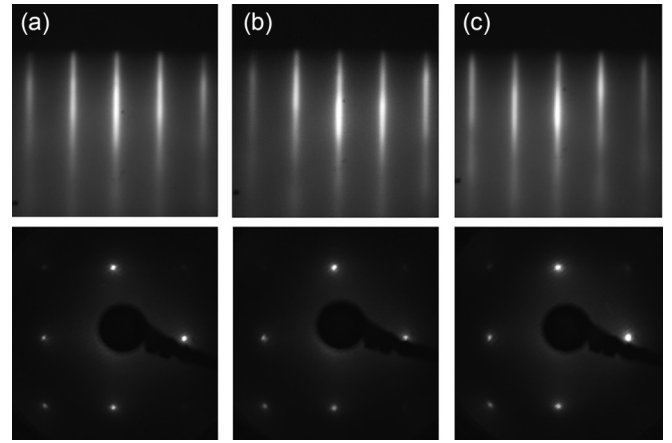


FIG. 1. RHEED and LEED images of the Fe_xTe films grown on SrTiO_3 (001) at an Fe flux rate of 1 $\text{\AA}/\text{min}$ and a Te flux rate of about 4 $\text{\AA}/\text{min}$ (Fe/Te flux rate ratio ≈ 0.25) with substrate temperatures of (a) 230°C , (b) 250°C , and (c) 300°C .

diffraction images are displayed in Fig. 1. For all substrate temperatures, the RHEED patterns are nicely streaked, indicating epitaxial Fe_xTe growth with smooth surface structure. Using the SrTiO_3 RHEED image as a reference, we derive an in-plane lattice parameter of about 3.8 $\text{\AA}$ for the Fe_xTe films, which is in good agreement with the bulk values for the short axes of the tetragonal structure reported in the literature [20]. Also, the LEED images exhibit sharp features. The spots have the expected fourfold symmetry revealing a good in-plane order. For the Fe_xTe film grown at a substrate temperature of 250°C , the images appear to be slightly crisper indicating the best crystallinity.

Using this optimized substrate temperature of 250°C , a series of Fe_xTe thin films was deposited at different Fe/Te evaporation rate ratios with the iron flux rate set at 1 $\text{\AA}/\text{min}$ while the tellurium flux rate was varied between 2.78 and 3.54 $\text{\AA}/\text{min}$ (Fe/Te flux rate ratios ranging from 0.36 to 0.28). Example RHEED images are shown in Fig. 2. The sharp RHEED streaks indicate a two-dimensional epitaxial growth, and the distinct fourfold symmetry of the LEED patterns reveals a single-phase and single-domain crystallization for all samples. Within the accuracy of the electron diffraction experiments, we observe no significant structural changes across the series grown at different tellurium rates.

For all films, the intensity of the specular RHEED spot shows time-dependent oscillations characteristic of layer-by-layer growth, displayed in Fig. 3(a). The oscillation periods, which correspond to the time for the deposition of one monolayer, vary between 88 to 121 s for the different films grown at 250°C , indicating a faster Fe_xTe growth rate for higher tellurium rates, i.e., smaller Fe/Te flux rate ratios. In Fig. 3(b), the reciprocal oscillation periods are summarized and plotted as a function of the Te evaporation rate. The observed linear trend indicates that the growth is determined by the supplied tellurium. At the substrate temperature of 250°C , most of the tellurium is incorporated into the layers, there is no significant reevaporation during the deposition.

To further characterize the structural properties, *ex situ* x-ray diffraction experiments were performed on the film

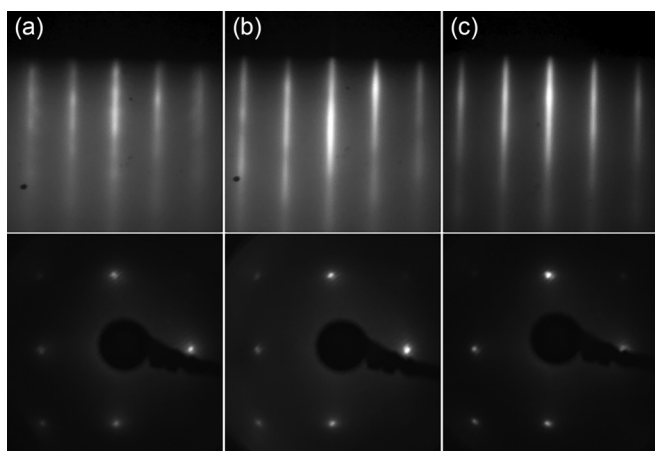


FIG. 2. RHEED and LEED images of the Fe_xTe films grown on SrTiO_3 (001) at a substrate temperature of 250°C and an Fe flux rate of $1 \text{ \AA}/\text{min}$ with Te flux rates of (a) $2.78 \text{ \AA}/\text{min}$ (Fe/Te flux rate ratio = 0.36), (b) $3.22 \text{ \AA}/\text{min}$ (Fe/Te flux rate ratio = 0.31), and (c) $3.54 \text{ \AA}/\text{min}$ (Fe/Te flux rate ratio = 0.28).

grown with a Te evaporation rate of $3.22 \text{ \AA}/\text{min}$ (the Fe flux rate is kept at $1 \text{ \AA}/\text{min}$), i.e., at an Fe/Te flux rate ratio of 0.31. The sample was capped with 12 nm of tellurium to prevent a degradation in air [34]. The XRD data are shown in Fig. 4. Aside from the diffraction peaks of the substrate, only the Fe_xTe peaks of the (00n) family of planes are observed in the XRD θ - 2θ scan which agree with the expected c -axis oriented tetragonal structure. The pronounced Laue fringes around the Fe_xTe peaks are a signature of high periodic order. The determined out-of-plane lattice constant of about $6.29 \text{ \AA}$ is slightly larger than the reported bulk values which could be related to a different Fe/Te composition which has been shown to influence the lattice parameters of bulk samples [20]. The ϕ scan around the Fe_xTe (023) reflection with its four peaks separated by 90° confirms the expected fourfold symmetry and the absence of in-plane rotated domains, and thus the growth of monocrystalline Fe_xTe films.

The composition of all Fe_xTe films was investigated by x-ray absorption and photoelectron spectroscopy making use of the fact that the intensity of the XAS absorption edges and XPS core levels is proportional to the concentration of the given element [35,36]. By evaluating the ratios of the peak areas of the Te M_5 and Fe $L_{2,3}$ XAS edges, as well as the Fe $3p$ and Te $4d$ XPS core levels, which we will show later, we determine the compositions of the films. A single-crystal bulk sample with known composition of $\text{Fe}_{1.13}\text{Te}$ is used as reference, thereby avoiding systematic errors due to photoionization cross sections or instrumental parameters. A summary of the obtained Fe/Te ratios for all samples is shown in Fig. 5 along with the corresponding Fe/Te flux rate ratios as measured by the quartz crystal monitor prior to deposition. The compositions of the films cover a range of Fe/Te ≈ 0.89 – 1.30 based on XAS (in red), and Fe/Te ≈ 0.74 – 1.27 based on XPS (in black). The two methods yield similar and consistent results. Nevertheless, the XPS values are systematically somewhat lower than the XAS results which might be related to the termination of the film growth and the surface sensitivity

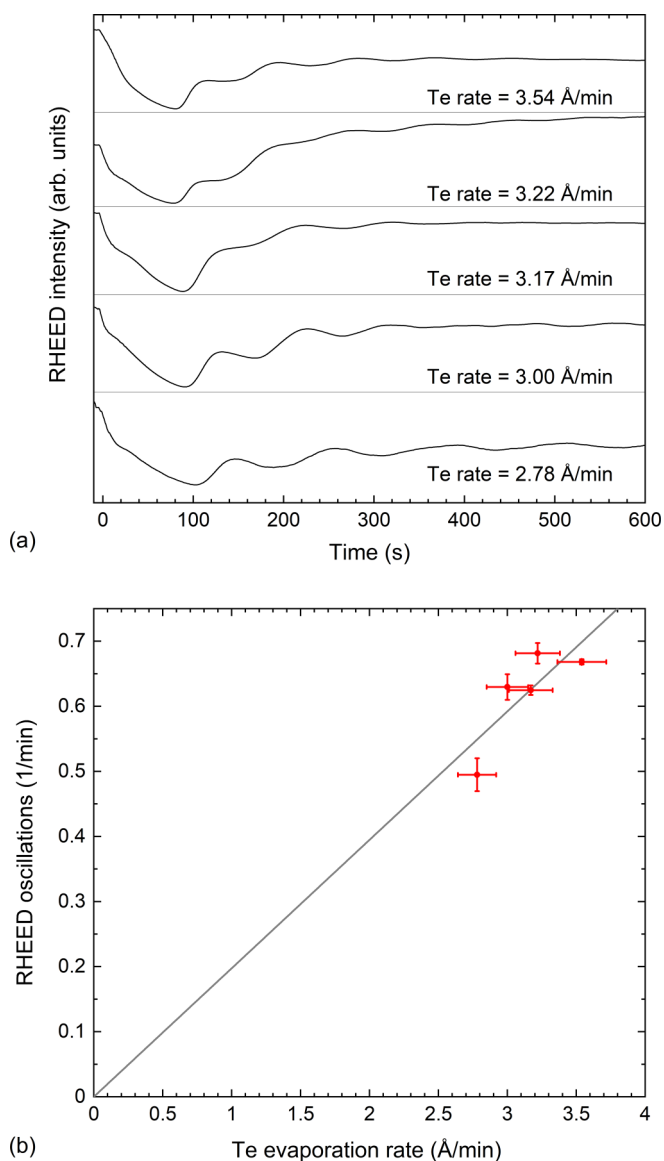


FIG. 3. (a) Time-dependent oscillations of the RHEED intensity for Fe_xTe films grown at various Te evaporation rates on SrTiO_3 (001) at a substrate temperature of 250°C . The shutter of the Fe effusion cell was opened at zero, immediately after the Te shutter. (b) Reciprocal period of the RHEED oscillations as a function of the Te evaporation rate. The gray line is a linear fit of the data with the intercept fixed at zero.

of the XPS measurement. In the following, the values of the more bulk-sensitive XAS measurements are used, for which the film grown at an Fe/Te flux rate ratio of 0.31 has a nearly ideal composition with Fe/Te ≈ 1.00 . The overall linear trend of the XAS and XPS results indicates that the composition is largely controlled by the tellurium rate, confirming that most of the tellurium is incorporated into the film, as already deduced from the RHEED oscillations (Fig. 3). Remarkably, despite the broad variety of compositions from Fe deficient to Fe rich, the electron diffraction results (Fig. 2) show no structural changes, suggesting that it may indeed be possible to stabilize a wider range of compositions in thin films than in bulk, in particular the ideal $\text{Fe}_{1.00}\text{Te}$ form, which is not

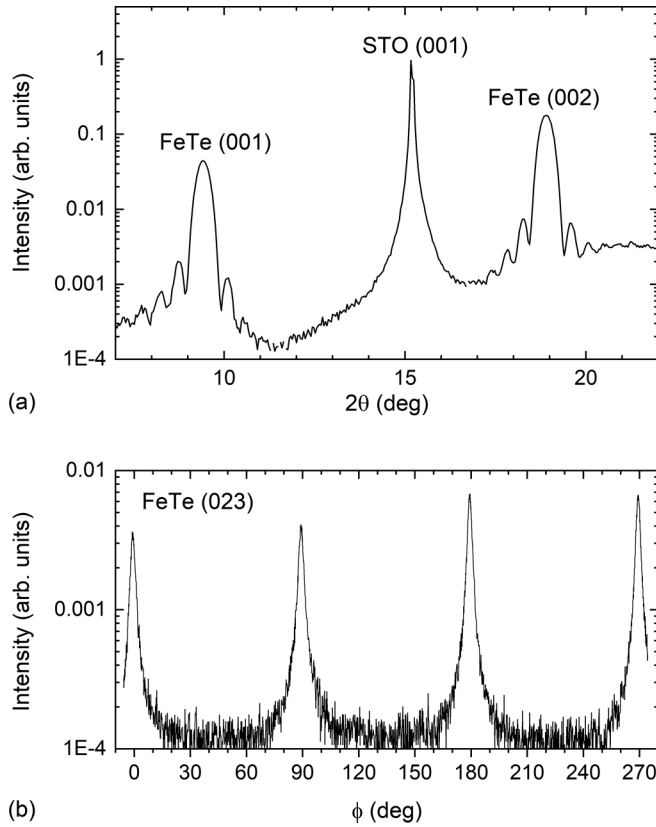


FIG. 4. XRD measurements of the film grown at Fe/Te flux rate ratio of 0.31. (a) θ - 2θ scan and (b) ϕ scan around the FeTe (023) reflection. The data were collected at $\lambda = 1.0332 \text{ \AA}$.

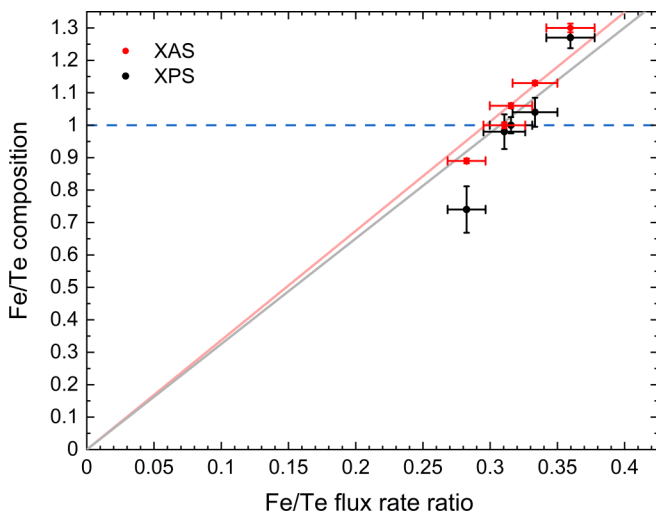


FIG. 5. Fe/Te ratios determined by XAS and XPS as a function of the Fe/Te flux rate ratios measured by the quartz crystal monitor prior to deposition. The compositions were derived from the peak areas of the Fe $L_{2,3}$ and Te M_5 XAS edges and of the Fe $3p$ and Te $4d$ XPS core levels after subtraction of a steplike background from the XAS data [37] and a Shirley-type background from the XPS data [38]. The dashed blue line indicates the ideal Fe/Te = 1 composition. The red (gray) line is a linear fit of the XAS (XPS) data with the intercept fixed at zero.

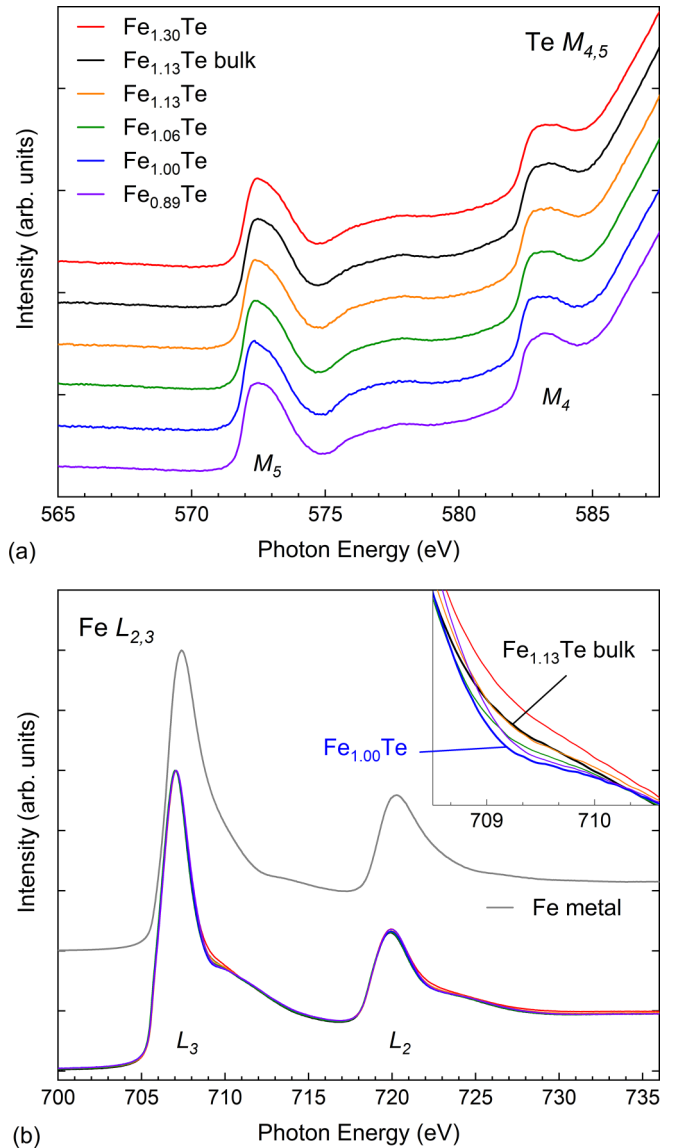


FIG. 6. XAS spectra of Fe_xTe films and Fe_{1.13}Te bulk reference (black). (a) Te $M_{4,5}$ edges, (b) Fe $L_{2,3}$ edges with Fe metal reference (gray). The spectra are normalized to the Te M_5 and Fe L_3 edge intensities, respectively. The Te spectra are vertically shifted for better visibility.

possible to synthesize as a bulk material. The fact that both the Fe_xTe growth rate and the composition are determined by the Te supply, while the overall structure of the Te sublattice is preserved, suggests that the films are prepared in a Te-limited growth regime. This is in contrast to other MBE studies that use Fe-limited conditions [29–31].

B. Spectroscopic analysis

We now analyze the spectra of the films with different Fe/Te compositions in more detail. The Te $M_{4,5}$ and Fe $L_{2,3}$ absorption edges are shown in Fig. 6. For comparison, we include the measurements of the Fe_{1.13}Te single crystal (in black). The Te $M_{4,5}$ spectra ($3d \rightarrow 5p$ transitions) have generally similar shapes, only the film with low Fe content has slightly more rounded absorption peaks. Also, the

Fe $L_{2,3}$ spectra ($2p \rightarrow 3d$ transitions) are comparable across the series. They feature mainly the two absorption lines (L_3 at 707 eV and L_2 at 720 eV). At first glance, the spectra have similarities to Fe metal, but the Fe_xTe lines are narrower and show more pronounced shoulders above the main lines. These sharper spectral features indicate that the Fe $3d$ electrons in Fe_xTe are not as itinerant as in the Fe metal. On the other hand, the Fe_xTe absorption lines are wider and the multiplet features are not as sharp and visible as in Fe^{2+} oxide compounds such as FeWO_4 [39], which are strongly correlated materials. In fact, the Fe_xTe spectra are reminiscent of Fe-based pnictides, which have been described as weakly correlated materials [40].

Beyond the overall similarities of the Fe absorption spectra, however, there are small but noticeable differences depending on the composition of the Fe_xTe samples. We see a systematic variation of the features on the higher photon energy sides of the Fe $L_{2,3}$ edges, shown enlarged for the L_3 edge in the inset. The film with $\text{Fe/Te} \approx 1$ composition (in blue) has at 709.2-eV photon energy a clear separation between main line and shoulder, which is less pronounced for the samples with lower and higher Fe contents, and is significantly smeared out for the film with the largest off-stoichiometry ($\text{Fe}_{1.30}\text{Te}$, in red). A similar trend is observed for the L_2 edges. The spectrum of the bulk reference sample (in black) fits well with the composition-dependent trend of the films. The change in the feature at 709 eV has been discussed for $\text{FeSe}_{1-y}\text{Te}_y$ compounds and has been associated with variations in the strength of the interaction between the Fe $3d$ and chalcogen p states [13,41].

In addition to the XAS analysis, we have also performed x-ray photoelectron spectroscopy measurements using a photon energy of 1000 eV. The wide scans (not shown here) reveal only the core levels of iron and tellurium, in particular the oxygen level is below the detection limit, confirming the high degree of purity of the samples. In Fig. 7, the Fe $3p$ and Te $4d$ core levels are shown. The intensities of the core levels reflect the composition as shown in Fig. 5. We see a clear increase of the Fe intensity and decrease of the Te intensity for the samples with higher Fe content. While the shape and the position of the Fe $3p$ peaks show negligible or tiny changes across the series, the Te $4d$ peaks clearly shift to higher binding energies for the larger Fe contents [see also enlarged Te $4d_{5/2}$ region in Fig. 7(c)]. This suggests that the excess iron introduces more charge into the system, leading to an overall shift of the narrow core levels of the noncorrelated tellurium to higher binding energies (we note that for the correlated Fe, a change in the electron number can be accompanied by the transfer of spectral weight to other energies, which in view of the broad spectral features of the Fe $3p$, results in the observed tiny changes of the line shape). In addition to the shifts in the tellurium core levels, the peak width also varies. The sharpest peak is observed for the film grown at Fe/Te flux rate ratio of 0.31 (in blue). Its position is marked by the blue arrow. The peaks become broader for higher and lower Fe contents with larger peak widths for larger off-stoichiometries. For the high Fe contents, the Te $4d$ states become double-peak-like with an additional contribution at higher binding energies marked by the red arrow for the Te $4d_{5/2}$, indicating that part of the tellurium feels now the excess iron which has a

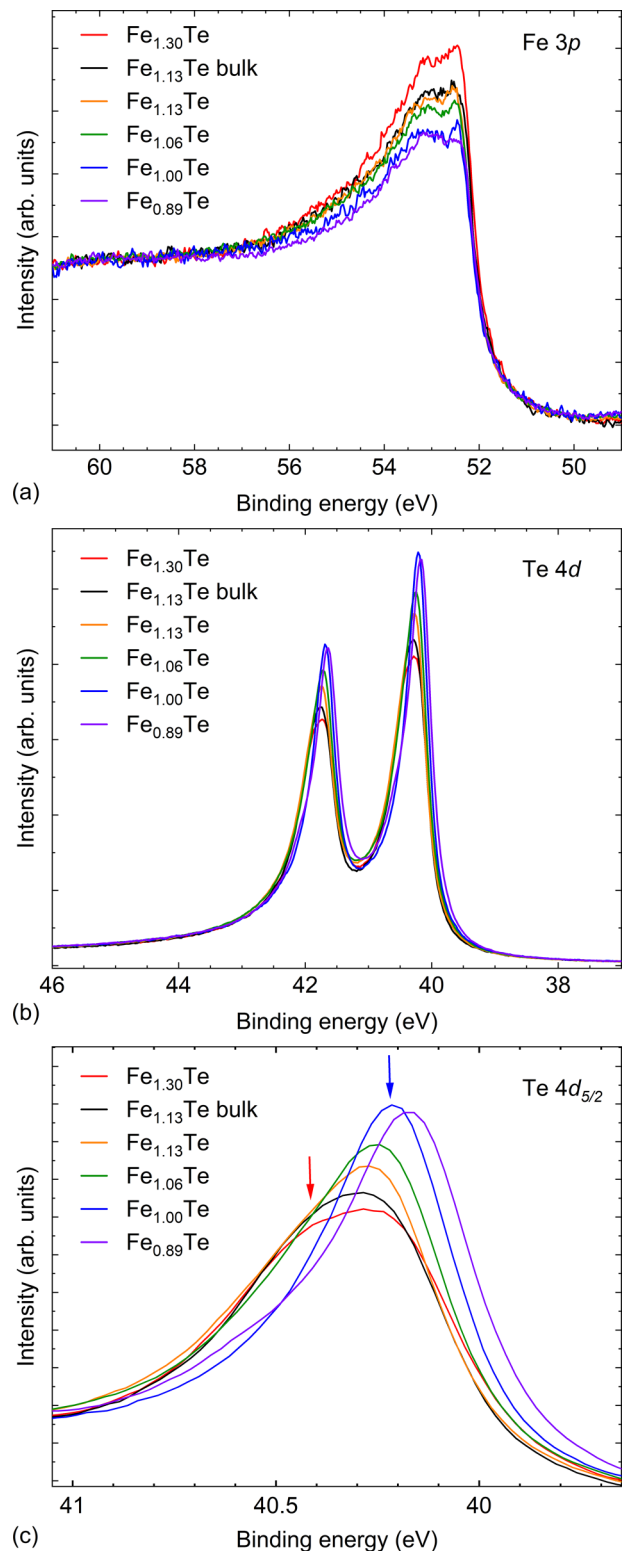


FIG. 7. XPS core-level spectra of Fe_xTe films and $\text{Fe}_{1.13}\text{Te}$ bulk reference. (a) Fe $3p$, (b) Te $4d$, and (c) zoom to the Te $4d_{5/2}$ region. The spectra are normalized to the background.

different local environment. And also the peaks of the film with low Fe content are broadened revealing that some part of the tellurium experiences vacancies. These results suggest that the film with the sharpest Te $4d$ peaks has only one

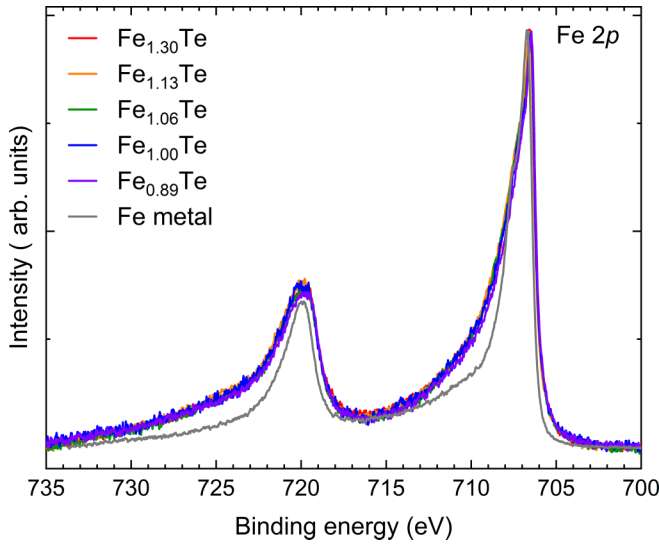


FIG. 8. Fe 2p XPS core level spectra of Fe_xTe films and Fe metal reference. The spectra are normalized to the highest intensity peak after Shirley-type background subtraction.

Fe-Te environment, i.e., a near-stoichiometric composition, supporting the Fe/Te ≈ 1.00 result of the XAS composition analysis. Again, the spectrum of the bulk reference sample fits well with the composition-dependent trend of the films. In particular, the $\text{Fe}_{1.13}\text{Te}$ bulk has the double peak that the $\text{Fe}_{1.00}\text{Te}$ film does not have.

Figure 8 displays the deeper iron core levels, the Fe 2p states. Similar to the Fe 3p states, the shape and position show no significant dependence on composition. The Fe 2p states are more than 2 eV lower in binding energy compared to Fe^{2+} oxide compounds [42], but rather very close to the Fe metal reference (in gray). While the Fe metal spectrum consists of two very narrow main lines corresponding to the spin-orbit split $2p_{3/2}$ and $2p_{1/2}$ states, the Fe_xTe peaks are slightly wider. Furthermore, the Fe_xTe spectra show additional intensity at the higher binding energy sides of the main peaks, which coincides with the positions of the satellites in correlated iron oxides (~ 5 – 6 eV above the main lines) (see, e.g., FeWO_4 [42]), indicating once more that correlation effects may not be negligible in FeTe.

The valence band region of the films is shown in Fig. 9 together with the $\text{Fe}_{1.13}\text{Te}$ bulk reference. The valence band spectra primarily exhibit two features, a narrow peak close to the Fermi level at binding energies of about 0.4–0.5 eV and a broader intensity distribution with a maximum at about 3.2 eV. All spectra have a clear and similar Fermi cutoff, revealing the metallic character of the samples. As the Fe content increases, the narrow peak changes, becoming more intense and broader, while the higher-energy feature remains almost unaffected. This suggests that the states close to the Fermi level are related to the iron which is in agreement with theory. Density functional theory band structure calculations

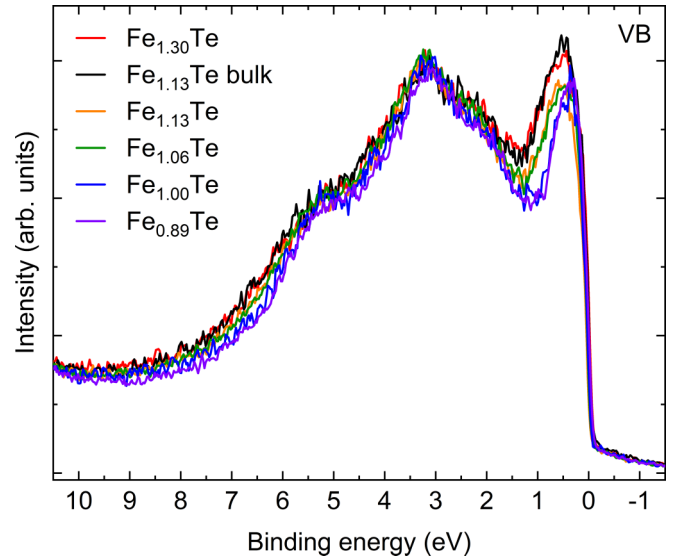


FIG. 9. XPS valence band (VB) spectra of Fe_xTe films and $\text{Fe}_{1.13}\text{Te}$ bulk reference. The spectra are normalized to the background at about 10.3 eV.

predict that the narrow feature originates from states of almost pure Fe 3d orbital character, whereas the feature at about 3.2 eV reflects states with strongly hybridized Fe 3d and Te 5p character [43,44].

IV. CONCLUSIONS

Fe_xTe films have been successfully synthesized by molecular beam epitaxy under Te-limited conditions. The preparation on SrTiO_3 (001) substrates yields epitaxial, monocrystalline films growing in a layer-by-layer fashion. By varying the Te evaporation rate, epitaxial Fe_xTe films with a wide range of compositions of $x \approx 0.89$ – 1.30 were obtained while maintaining the crystalline order. The electronic structure and its composition-dependent changes were systematically studied by *in situ* x-ray absorption and x-ray photoelectron spectroscopy on freshly grown, clean surfaces. Our measurements show that the spectral features are most pronounced and sharpest for the film with optimized Fe/Te ratio, also in comparison to the $\text{Fe}_{1.13}\text{Te}$ bulk reference. This suggests that the ideal $\text{Fe}_{1.00}\text{Te}$, although not possible as a bulk material, can be prepared in thin-film form, opening up new opportunities for future research.

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