Microscopic analysis of the chemical reaction between Fe(Te, Se) thin films and underlying CaF$_2$

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Abstract
To understand the chemical reaction at the interface of Fe(Te, Se) and CaF$_2$ materials, we used transmission electron microscopy to analyze five types of Fe(Te, Se) superconducting thin films prepared on different types of substrate: two on a CaF$_2$ substrate, one on a CaF$_2$ substrate with a CaF$_2$ buffer layer, one on a CaF$_2$ substrate with an FeSe buffer layer, and one on a LaAlO$_3$ substrate with a CaF$_2$ buffer layer. Energy-dispersive x-ray spectroscopy analysis revealed a potential interdiffusion between fluorine and selenium that plays a significant role in the variation of the lattice parameters. We conclude that the lattice parameters of the Fe(Te, Se) thin films are primarily determined by the chemical substitution of anions, while the lattice mismatch plays a secondary role.

1. Introduction
Following the discovery of superconductivity in iron pnictide materials [1], a considerable number of experiments have been performed to fabricate thin films and single crystals in pursuit of higher critical temperatures ($T_C$). These new superconductors have been categorized into five major families: the ‘1111 family’, which includes the first material, LaFeAsO$_{0.89}$F$_{0.11}$, and its derivatives; the ‘111 family’, which includes LiFeAs [2]; the ‘122 family’, which includes BaFe$_2$As$_2$ [3]; the ‘11 family’, which includes FeTe$_{1-x}$Se$_x$ [4]; and the ‘perovskite family’, which includes the perovskite-containing compound Sr$_2$ScO$_3$FeAs [5]. Among these families of materials, the ‘11’ family has the simplest structure, which is an advantage for practical applications. Although the $T_C$ of bulk FeSe is rather low, approximately 8 K, the ‘11’ compound was reported to exhibit a strong pressure dependence [6] and was subsequently reported to exhibit $T_C = 37$ K under a high pressure of approximately 7 GPa [7, 8]. Therefore, applying lattice strain using a lattice mismatch between the substrates and the thin films of these superconducting materials is of particular interest to researchers. Bellingeri et al reported that the dependence of $T_C$ on the thickness of the film is explained by a change in the strain effect, and presented the highest reported $T_C$ of 21 K as evidence that strain can change the $T_C$ [9]. Mele et al have reported that the upper critical field, $B_C^2 \parallel (0)$, can be as high as 60 T, even for a low-$T_C$ Fe(Te, S) film with a $T_C$ of 4 K [10], indicating that the ‘11’ superconducting films have the potential to be used in low-temperature applications.

In early studies on thin-film growth, conventional oxide substrates were widely used to grow ‘11’ films. Several research groups have reported that the $T_C$ of the film strongly depends on the oxide substrate materials [11–15]. We observed that the $T_C$ of the ‘11’ film strongly depends on the amount of oxygen that penetrates into the film from the oxide substrate [16, 17]. Based on these findings, we have proposed the use of CaF$_2$ as a substrate and have succeeded
in improving the $T_C$ and other parameters [18]. Note that, in the case of the films grown on CaF$_2$ substrates, the $a$-axis becomes shorter while the $c$-axis length simultaneously becomes longer than that in the bulk crystal [19]. Because the $a$-axis length of CaF$_2$ is considerably longer than that of bulk FeTe$_{0.5}$Se$_{0.5}$, this lattice deformation cannot be explained by a conventional epitaxial strain effect, and thus an explanation for the suitability of CaF$_2$ over oxide substrates has remained unclear. In the present manuscript, we prepared Fe(Th, Se) thin films on different underlying structures of CaF$_2$ and analyzed the microstructures at the interface of five films (film A to film E) by transmission electron microscopy (TEM). We will discuss the variation of the microstructure as a function of slight variations in the chemical composition of the Fe(Th, Se) superconducting films on the CaF$_2$ substrate. Then, we will discuss the influence on the superconducting films of varying the underlying substrate structure while maintaining the same Fe(Th, Se) composition. Finally, we will propose the most likely mechanism for the lattice deformation and $T_C$ variation by using microstructure analyses when using CaF$_2$ substrates for the ‘11’ superconducting films.

### 2. Experimental procedures

We have previously discussed FeTe$_{0.5}$Se$_{0.5}$ thin films [15–18], but in this study we newly prepared four FeTe$_{0.6}$Se$_{0.4}$, thin films to keep the film composition slightly away from the boundary to the region in which the miscibility gap exists (Te/Se < 0.5/0.5). All the thin films were deposited using the pulsed-laser deposition (PLD) method with a KrF excimer laser ($\lambda = 248$ nm) using polycrystalline targets with a nominal composition of Fe:Se:Te = 1.0:0.4:0.6. Buffer layers were also deposited using polycrystalline CaF$_2$ and an FeSe target. The deposition temperatures for Fe(Th, Se), FeSe, and CaF$_2$ were 280 °C, 280 °C, and 340 °C, respectively. The repetition frequency and energy of the laser were 10 Hz and 300 mJ, respectively. The film preparation has been described in detail elsewhere [15, 17]. The out-of-plane crystal orientations were characterized by x-ray diffraction. The temperature dependence of the resistivity was measured using the standard four-probe method.

Table 1 summarizes the specifications of the five films. Film A is an FeTe$_{0.5}$Se$_{0.5}$ film grown on a bare CaF$_2$ (100) substrate and is identical to sample A in [18]. Film B is an FeTe$_{0.6}$Se$_{0.4}$ film grown on a bare CaF$_2$ (100) substrate. Films C and D are FeTe$_{0.6}$Se$_{0.4}$ films grown on a CaF$_2$ (100) substrate with CaF$_2$ and FeSe inserted between the film and the substrate, respectively. Film E is an FeTe$_{0.6}$Se$_{0.4}$ film grown on a LaAlO$_3$ (100) substrate with an inserted CaF$_2$ buffer layer. The difference between films A and B is the chemical composition ratio of Te and Se in the films. According to the EDX analyses, it is confirmed that the Se content in the film decrease with decreasing the Se content in the target. However, the Se composition in the film is approximately 1.4 times larger than the nominal Se composition of the target. All films are described by the nominal composition of the target in this paper because of the uncertainty of quantitative in EDX analyses.

Samples for TEM analyses were prepared by cutting and milling using a focused ion beam (FIB) according to the so-called micro-bridge sampling technique. The microstructures of these samples were examined with a JEOL TEM-2100F microscope with an energy-dispersive x-ray spectrometer (EDX). The chemical composition ratio of each element at each point is estimated as an atomic percentage, in which 100% represents the sum of all constituent elements of the substrate, buffer layer, and film. Nanobeam electron diffraction (NBD) experiments were performed to evaluate local structures in the interfacial area between the films and the substrates. An incident electron beam was theoretically focused to cover a spot with a diameter of 1 nm in the NBD experiments.

### 3. Results and discussion

Figure 1 shows the temperature dependence of the resistivity of films A–E. These films exhibited an onset of superconductivity, $T_{C_{\text{onset}}}$, at 16.6, 14.9, 13.7, 14.4, and 13.0 K, respectively. The $T_{C_{\text{onset}}}$ of film A exhibited the highest $T_C$, which is reasonable because this film had a different Se/Te ratio. The $T_{C_{\text{onset}}}$ of the other films was approximately 14 K, which is not an extremely low value for FeTe$_{0.6}$Se$_{0.4}$.

In the subsequent paragraphs, we will present the details of the TEM observations of each film. A cross-sectional scanning TEM (STEM) image of film A is presented in figure 2(a). A high-resolution cross-sectional TEM image of

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**Table 1. Sample specifications and growth conditions for films A, B, C, D, and E. Film A was identical to sample A in [18], while the other films were newly prepared.**

| Nominal composition of film | Substrate | Deposition temperature of film/(buffer) (°C) | Thickness of film/(buffer) (nm) | $T_{C_{\text{onset}}}$ (K) | $a$-axis length (nm) | $c$-axis length (nm) | $c/a$ |
|----------------------------|-----------|---------------------------------------------|-------------------------------|--------------------------|---------------------|---------------------|-------|
| FeTe$_{0.5}$Se$_{0.5}$     | CaF$_2$   | 280                                         | 115                           | 16.6                     | 0.376               | 0.594               | 1.579 |
| FeTe$_{0.6}$Se$_{0.4}$     | CaF$_2$   | 280                                         | 100                           | 14.9                     | 0.376               | 0.601               | 1.597 |
| FeTe$_{0.6}$Se$_{0.4}$     | CaF$_2$/CaF$_2$ buffer | 280/(340) | 200/(75) | 13.7                   | 0.377               | 0.605               | 1.604 |
| FeTe$_{0.6}$Se$_{0.4}$     | CaF$_2$/FeSe buffer | 280/(280) | 130/(170) | 14.4                   | 0.374               | 0.605               | 1.615 |
| FeTe$_{0.6}$Se$_{0.4}$     | LaAlO$_3$/CaF$_2$ buffer | 280/(340) | 165/(60)  | 13.0                   | 0.375               | 0.605               | 1.611 |
Figure 1. Temperature dependence of the resistivity of films A–E. Inset: the expanded figure below 20 K.

Figure 2. Cross-sectional STEM image (a), high-resolution TEM images near the interface region (b), and SAED (c) for film A. The yellow square area shown in (a) is magnified in (b). The interface is indicated with a yellow dashed line in (b). The marks ‘F’ and ‘S’ in the SAED pattern correspond to the film and substrate, respectively.

A cross-sectional STEM image of film C is shown in figure 4(a). The interface between FeTe$_{0.6}$Se$_{0.4}$ and the CaF$_2$ buffer layer exhibited a peculiar structure. There were many triangular shapes that were several tens of nanometers in length at this interface, indicating that the structure of this type of surface overlapped along the direction incident to the electron beam. Surprisingly, the surface of the superconducting film exhibited excellent flatness, even though the surfaces of the underlying layers were extremely rough. Therefore, the ‘11’ superconductors can grow two dimensionally, irrespective of the degree of surface flatness of the underlying layer.

Cross-sectional, high-resolution TEM images near the two interfaces of film C, corresponding to the square areas I and II shown in figure 4(a), are shown in figures 4(b) and (c), respectively. The CaF$_2$ buffer layer and the CaF$_2$ substrate are well ordered due to homoepitaxial growth. The interface between FeTe$_{0.6}$Se$_{0.4}$ and CaF$_2$ is more complicated. The

Film A, which corresponds to the area indicated in figure 2(a), and a selected-area electron diffraction (SAED) pattern are presented in figures 2(b) and (c), respectively. A yellow dashed line is drawn at the interface in figure 2(a). A bright layer that was approximately 5 nm in width extended from the interface between the CaF$_2$ substrate and the superconducting film. This region was not amorphous, as confirmed by the SAED pattern. According to figure 2(c), FeTe$_{0.5}$Se$_{0.5}$[110]∥CaF$_2$ [100] and FeTe$_{0.5}$Se$_{0.5}$(001)∥CaF$_2$ (001), and the lengths of the a- and c-axes of film A are 0.376 and 0.594 nm, respectively. Figure 3 shows the same set of images for film B as shown for film A: a cross-sectional STEM image, a high-resolution TEM image, and an SAED pattern. A yellow dashed line is drawn at the interface in figure 3(a). The interface between the CaF$_2$ substrate and the FeTe$_{0.6}$Se$_{0.4}$ superconducting film was almost identical to that of film A. According to figure 3(c), FeTe$_{0.6}$Se$_{0.4}$[110]∥CaF$_2$ [100] and FeTe$_{0.6}$Se$_{0.4}$(001)∥CaF$_2$(001), which is the same as between CaF$_2$ and film A. The a- and c-axis lengths were estimated to be 0.376 and 0.601 nm, respectively. The a-axis length was almost the same as that of film A, while the c-axis length was longer. These changes in the a- and c-axis lengths display a trend similar to that observed for the changes in the bulk samples [20], indicating that the main reason behind the differences observed in films A and B is simply the relative proportions of Te and Se.
Figure 3. Cross-sectional STEM image (a), high-resolution TEM images near the interface region (b), and SAED (c) for film B. The yellow square area shown in (a) is magnified in (b). The interface is indicated with a yellow dashed line in (b). The marks ‘F’ and ‘S’ in the SAED pattern correspond to the film and substrate, respectively.

yellow dashed lines are drawn perpendicular to the equivalent direction of CaF$_2$ [111] in figure 4(c), which indicates that the plane corresponding to the yellow dashed lines is equivalent to CaF$_2$ (111). In other words, the pyramidal structures surrounded by the (111) planes are observed as an overlapped image. The preferential crystal growth direction of CaF$_2$ was reported to be along [110] [21]. In this case, the pyramidal structure surrounded by the (111) planes is known to be formed when CaF$_2$ has the c-axis orientation.

Figure 4. Cross-sectional STEM image (a), high-resolution TEM images near two interface regions (b), (c), and SAED (d) for film C. The yellow square areas I and II shown in (a) are magnified in (b) and (c), respectively. (b) and (c) are the interfaces between the CaF$_2$ substrate and the CaF$_2$ buffer layer and between the CaF$_2$ buffer layer and the FeTe$_{0.6}$Se$_{0.4}$ superconducting film, respectively. The interfaces are indicated as yellow dashed lines in (b) and (c). The marks ‘F’ and ‘B’ in the SAED pattern correspond to the film and buffer layers, respectively.
Note that the ‘bright’ layer observed at the interface of film A was not detected in film C. Although a thin reaction layer existed at the interface, surface irregularities greater than approximately 10 nm in height concealed a thin layer with an approximate thickness of 5 nm. Figure 4(d) presents the SAED pattern at the interface between the CaF$_2$ buffer layer and the FeTe$_{0.6}$Se$_{0.4}$ superconducting film. According to the SAED pattern observed, FeTe$_{0.6}$Se$_{0.4}$ [100] || CaF$_2$ [110] and FeTe$_{0.6}$Se$_{0.4}$ (001) || CaF$_2$ (001), and the $a$- and $c$-axis lengths were estimated to be 0.377 and 0.605 nm, respectively.

Another interesting finding is that the FeTe$_{0.6}$Se$_{0.4}$ layer begins to grow immediately above the bottom of the valley of CaF$_2$ buffer layers. This result suggests that the growth direction of Fe(Te, Se) is also strongly governed by the (111) facet of CaF$_2$. This may indicate the presence of an intimate epitaxial relationship between CaF$_2$ and Fe(Te, Se) and suggest the possibility of growing non-$c$-axis oriented ‘11’ films.

A cross-sectional STEM image of film D is shown in figure 5(a). Although the interface between the FeSe buffer layer and the FeTe$_{0.6}$Se$_{0.4}$ film is not clear, slight but detectable differences in the contrast change in each layer can differentiate the two layers. Cross-sectional, high-resolution TEM images near the two interfaces of film D, which correspond to the square areas I and II shown in figure 5(a), are shown in figures 5(b) and (c), respectively. Each interface is marked by yellow dashed lines. A bright, thin layer with a thickness of approximately 5 nm was observed inside the CaF$_2$ substrate, as was observed for films A and B, indicating that a similar reaction occurred at the interface of the CaF$_2$ substrate. The interface between FeSe and FeTe$_{0.6}$Se$_{0.4}$ is flat and well ordered. The high-resolution TEM images of the FeSe buffer layer and the FeTe$_{0.6}$Se$_{0.4}$ superconducting layer, which correspond to the square areas III and IV in figure 5(a), are shown in figures 6(a) and (b), respectively. The image contrast of the FeSe buffer layer shown in figure 6(a) appears rather inhomogeneous compared to that of the FeTe$_{0.6}$Se$_{0.4}$ films shown in figure 6(b). A slight crystal distortion or crystal rotation is known to frequently result in an uneven contrast in high-resolution TEM images. Figure 6 indicates that the crystal structure of FeTe$_{0.6}$Se$_{0.4}$ is more ordered than that of FeSe. The difference in the lattice parameters between FeSe and FeTe$_{0.6}$Se$_{0.4}$ appears to affect the morphology of the materials at the nanometer scale. Figure 5(d) shows the SAED pattern at the interface between the FeSe buffer layer and the FeTe$_{0.6}$Se$_{0.4}$ film. According to the SAED pattern, FeTe$_{0.6}$Se$_{0.4}$ [100] || FeSe [100] and FeTe$_{0.6}$Se$_{0.4}$ (001) || FeSe (001), and the $a$- and $c$-axis lengths of the FeSe buffer layer and the FeTe$_{0.6}$Se$_{0.4}$ superconducting layer were estimated to be 0.371 and 0.551 nm and 0.375 and 0.604 nm, respectively. Furthermore, the diffraction spots from FeSe were slightly more dispersed than those from FeTe$_{0.6}$Se$_{0.4}$, which is consistent with the TEM results. We also performed a reciprocal space mapping (RSM) of this particular film, which supports both the in-plane and out-of-plane alignment mentioned above and gave $a$- and $c$-axis lengths for FeSe of 0.3746 and 0.5582 nm, respectively, and for FeTe$_{0.6}$Se$_{0.4}$ of 0.3758 and 0.6083 nm, respectively, in good agreement with those estimated from SAED.

Figure 5. Cross-sectional STEM image (a), high-resolution TEM images near two interface regions (b), (c), and SAED (d) for film D. The yellow square areas I and II shown in (a) are magnified in (b) and (c), respectively. (a) and (b) are the interfaces between the CaF$_2$ substrate and the FeSe buffer layer and between the FeSe buffer layer and the FeTe$_{0.6}$Se$_{0.4}$ superconducting film, respectively. The interfaces are indicated with yellow dashed lines in (a) and (b). The marks ‘F’ and ‘B’ in the SAED pattern correspond to the film and buffer layers, respectively.
A nanobeam electron diffraction measurement in the region local crystallographic structure at this bright area, we made structure was observed in the CaF$_2$ substrate. It may be concluded that the amorphous region at the interface began forming after a sufficient nucleation of CaF$_2$. The yellow dashed lines in figure 7(c) correspond to CaF$_2$ (001) and CaF$_2$ (111). The surface structure of the CaF$_2$ buffer layer includes a pyramid surrounded by CaF$_2$ (111) facets, as observed for film C. Therefore, the bright thin layer at the surface of the CaF$_2$ buffer layer may be invisible for the same reason as stated for film C, in which surface irregularities concealed a thin layer potentially present at the surface. According to the SAED patterns, FeTe$_{0.6}$Se$_{0.4}$ [100] || CaF$_2$ [110] || LaAlO$_3$ [100] and FeTe$_{0.6}$Se$_{0.4}$ [001] || CaF$_2$ [001] || LaAlO$_3$ [100], and the a- and c-axis lengths of film E were estimated to be 0.375 and 0.605 nm, respectively.

Figures 9(a)–(e) present the EDX results for films A–E, respectively. Figure 9(f) presents the EDX result of the expanded area near the substrate interface for film D. In all films, the amount of fluorine in CaF$_2$ decreased closer to the interface. In film C, although the amount of fluorine was almost constant in the substrate, it decreased approaching the interface of the superconducting film (figure 9(c)). In film E, the amount of fluorine decreased approaching both interfaces below and above the CaF$_2$ buffer layers, as shown in figure 9(e). Specifically, at the interface between the CaF$_2$ buffer layer and the LaAlO$_3$ substrate, the presence of fluorine was clearly detected, but calcium was not detected in the amorphous layer in the top region of the substrate. Calcium fluoride is known to be a stable material, although the present result indicates that the fluorine ions are likely to move even at the relatively low temperature of 340 °C. This tendency is much more pronounced in the post-deposited CaF$_2$ buffer layer, possibly due to different surface conditions (the CaF$_2$ (111) facet is dominant in the CaF$_2$ buffer layer, whereas the CaF$_2$ (100) surface is dominant in the CaF$_2$ substrate) and/or the difference in the density of defects between the CaF$_2$ buffer layer and substrate.

Another interesting feature is observed for Se ions. Generalizing the observations in figures 9(a) and (b), the EDX signal from Se ions was present even at the interface between CaF$_2$ and Fe(Te, Se), while the signal from Te ions was rapidly lost at the same position. This strongly indicates that Se and Te behave differently and that the Se tends to penetrate into the CaF$_2$ substrate in films A and B. This tendency is also observed at the interface between CaF$_2$ and FeSe in film D as shown in figure 9(f). To summarize the EDX results, two types of atomic diffusion are suggested to occur: one for F$^-$ from CaF$_2$ to Fe(Se, Te) and one for Se$^{2-}$ from Fe(Se, Te) to CaF$_2$.

For the oxide substrates, the reaction layers definitely evolved in the superconducting films, as confirmed previously [16, 17]. In other words, oxygen penetrated into the film and perturbed the crystal structure of the superconducting film. The penetration of oxygen into Fe(Se, Te) induced...
significant disorder in the crystal structure of Fe(Te, Se) and thus was easily detected by TEM. Conversely, in the case of the fluoride substrates, the reaction layers were always observed at only one side of the interface: the CaF$_2$ layer side. It was difficult to precisely determine the number of fluorine ions in the superconducting films because the detection accuracy for fluorine ions was lower than that for any other element. However, according to the EDX results, it is reasonable to expect that the fluorine ions moved from the CaF$_2$ substrates to the Fe(Te, Se) films. Two scenarios are possible for the incorporation of fluorine ions: one is the F substitution of Se and the other is the intercalation of fluorine ions between adjacent Fe(Te, Se) layers.

The former scenario seems to be consistent with the EDX results. Figures 9(a) and (b) suggest that a certain number of selenium ions were present inside the CaF$_2$ substrates,
indicating mutual interdiffusion of Se$^{2-}$ and F$^-$ ions. As mentioned previously, the diffusion of Te ions was not detected by EDX in the present study. Thus, by considering the presence of well ordered epitaxial growth immediately above the substrate surface and the absence of any remarkable lattice disorder at the interface, we may expect that the substitution of fluorine ions for selenium ions occurs across CaF$_2$ substrates and Fe(Fe, Se) films. If the smaller F$^-$ ions (ionic radius = 0.119 nm) are substituted in the place of the larger Se$^{2-}$ ions (ionic radius = 0.184 nm), the lattice will be primarily compressed along the $a$-axis direction, most likely due to the smaller spacing within the anion layers along the in-plane direction. In this case, it would be reasonable to expect a resulting lattice expansion along the $c$-axis direction by Poisson’s effect.

By contrast, in the latter scenario of the intercalation of fluorine ions between adjacent Fe(Fe, Se) layers, we would expect the occurrence of a drastic expansion along the $c$-axis direction. The most likely position for the intercalated F$^-$ ions would be in between the adjacent Se$^{2-}$ layers, where the F$^-$ would be surrounded by anionic Se$^{2-}$ ions. In this case, the F$^-$ ion is likely to expand the $a$-axis length. As will be discussed later, the lattice parameters estimated from the SAED patterns suggest an empirical tendency for simultaneous compression along $a$ with expansion along $c$, increasing the favorability of the former Poisson-effect scenario. In the next paragraph, we will discuss this point in more detail.

The $T_C$ onset of the Fe11-based superconductors was reported to correlate to the ratio of the lattice lengths, $c/a$ [16]. Figure 10 shows the $a$- and $c$-axis lengths as a function of their ratio, $c/a$, as evaluated by SAED. Previous data for the FeTe$_{0.5}$Se$_{0.5}$ thin films on oxide substrates are also plotted in figure 10 for comparison. For the lattice parameters, the overall tendencies were similar to those revealed by x-ray diffraction studies [17]: when CaF$_2$-buffered substrates were used, the values of $c/a$ increased, the $a$-axis length became short, and the $c$-axis length became long. This result cannot be explained by a simple lattice-strain effect induced by the CaF$_2$ substrate; the $a$-axis length of the FeTe$_{0.6}$Se$_{0.4}$ bulk sample is 0.3798 nm and that of the CaF$_2$ crystal is 0.386 nm, which would instead induce a tensile strain into the superconducting films. The experimental results reveal that the $a$-axis length is in the range of 0.372–0.382 nm. This means that the FeTe$_{0.6}$Se$_{0.4}$ film shrinks by itself without experiencing an external tensile stress. Therefore, these results suggest that the chemical substitution between F$^-$ and Se$^{2-}$ drives the lattice deformation of FeTe$_{0.6}$Se$_{0.4}$ thin films when grown on CaF$_2$ substrates.

The effect of the buffer layers on lattice deformation was evaluated by comparing films prepared with or without a CaF$_2$ buffer layer. FeTe$_{0.6}$Se$_{0.4}$ superconducting films prepared on CaF$_2$ buffer layers had a similar or shorter range of $a$-axis lengths compared to FeTe$_{0.6}$Se$_{0.4}$ films prepared directly on CaF$_2$ substrates. By contrast, the $c$-axis length of the FeTe$_{0.6}$Se$_{0.4}$ superconducting thin films on the CaF$_2$ buffer layers was obviously longer than that of the FeTe$_{0.6}$Se$_{0.4}$ superconducting thin films on the CaF$_2$ substrate. Regardless of the clear increase in the $c$-axis length of the FeTe$_{0.6}$Se$_{0.4}$ films on the CaF$_2$ buffer layer, the $T_C$ onset slightly decreased, representing an inverse correlation between the lattice length and the $T_C$ onset.

The difference in the lattice lengths of the FeTe$_{0.6}$Se$_{0.4}$ superconducting thin films on the CaF$_2$ substrate and the buffer layer may be explained by the different surface conditions. The CaF$_2$ buffer layer exhibits a characteristic pyramidal structure. This morphology may facilitate ion diffusion because of the considerable number of passages along the grain boundaries and the wide contact area. The partial substitution of fluorine ions for selenium ions also influences the electronic structure. The electronic structure of the superconducting films on CaF$_2$ substrates will be investigated in the near future.

One may suspect the possible influence of excess Fe [22, 23]. Systems in which the $c$-axis length increases and the $a$-axis length decreases as excess Fe decreases have been reported [22, 23]. Furthermore, excess Fe has been shown to have a strong effect on superconductivity, where $T_C$ increases with decreasing excess Fe. In the present study, however, we confirmed that the effect of excess Fe was not significant. When films contain excess Fe, they exhibit an anomalous Hall effect [24]. We confirmed, however, that an anomalous Hall effect due to excess Fe was barely observed in the films in this study, and thus we can discuss the variation in lattice parameters and $T_C$ values without considering the effect of excess Fe.

4. Conclusions

The four types of substrate used to grow FeTe$_{0.6}$Se$_{0.4}$ superconducting films by PLD and their microstructures and ion distributions across the interface were analyzed by TEM and compared with the analysis of FeTe$_{0.5}$Se$_{0.5}$. The Fe11-based superconductors grew two dimensionally regardless of the morphology of the underlying layers.
Furthermore, the fluorine ions were found to move during film deposition. The strong possibility of fluorine ion incorporation in the Fe(Se, Te) films is supported not only by EDX analysis but also by the change in the lattice parameters, as estimated by SAED. The Poisson’s effect-type lattice deformation of Fe(Se, Te) films on CaF$_2$ substrates is indicative of the partial substitution of fluorine ions for selenium ions. It can be concluded that the lattice parameters of the Fe(Se, Te) thin films are primarily determined by the chemical substitution of anions, while the lattice mismatch plays a secondary role.
Therefore, fluoride substrates are more suitable as substrates for Fe11 superconducting films than oxide substrates due to the different chemical reaction at the interface.

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