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Substrate effect on structure and superconductivity in SmFeAs(O,F) epitaxial films

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ABSTRACT

Superconducting SmFeAs(O,F) films were prepared on various substrates by molecular beam epitaxy and subsequent fluorine diffusion from an overlayer of SmF_3. We have performed a detailed comparison of films on different substrates in the structure and superconductivity. In general, fluoride substrates are more suitable than oxide substrates in obtaining better superconductivity of SmFeAs(O,F) films. The best substrate so far is CaF_2, which yielded record high T_c, $T_c^{on}(T_c^{end})$ = 57.8 K (56.4 K). There is a clear correlation between T_c and epitaxial strain in SmFeAs(O,F) films on CaF_2: "the less epitaxial strain, the higher T_c". The implication of this correlation is briefly discussed.

1. Introduction

After 4 years since the recent discovery of high-T_c iron pnictides [1], worldwide intensive efforts have been made for film growth of these superconductors. At the beginning, epitaxial thin films of F-doped highest-T_c *RE*FeAs(O,F) (*RE*-1111, *RE* = rare-earth) phase appeared to be hard to produce, but at present high-quality epitaxial films of *RE*FeAs(O,F) have already been produced using molecular beam epitaxy (MBE) by Nagoya University group [2,3] and also by our group [4–6]. Employing CaF_2 as a substrate, T_c over 55 K has been achieved. In this article, we report on the substrate dependence of SmFeAs(O,F) films. We performed a systematic investigation on the structure and properties of superconducting SmFeAs(O,F) films grown by MBE on various substrates. The results indicated that fluoride substrates are more suitable than oxide substrates in obtaining better superconductivity of SmFeAs(O,F) films. The best substrate so far is CaF_2. On CaF_2, we see a trend that the T_c of the films decreases and the superconducting transition broadens as the films are more heavily distorted by epitaxial compressive strain.

2. Experimental

All the films were grown in the customer-designed MBE chamber (base pressure of $\approx 1 \times 10^{-9}$ Torr) equipped with the precise control systems for atomic beam fluxes. The details of our MBE growth of Fe-based superconductors is described in Refs. [4–6]. In brief, first, F-free SmFeAsO films were grown by coevaporating Sm, Fe, and As in oxygen atmosphere. The typical growth temperature was 650 °C. Subsequently F was diffused to the SmFeAsO films by depositing an overlayer of 200–300 Å thick SmF_3 at T_s = 650 °C and holding the films at the same temperature for 30 min. The substrates used for the growth were CaF_2 (001), SrF_2 (001), BaF_2 (001), *r*-cut Al_2O_3, $YAlO_3$ (110), $LaAlO_3$ (001), and MgO (001). The lattice parameters of these substrates are summarized in Table 1. The rate of Fe was 0.25–0.5 Å/s and the deposition for 5–10 min produced 1000–1700 Å thick films of SmFeAsO. The films were characterized by X-ray diffraction (XRD) using both two-circle and four-circle diffractometers and by resistivity vs. temperature (ρ–T) measurements. Sm(O,F) overlayers on F-diffused films did not become obstacle to transport measurements, because probe pins, which we pressed to films, probably pierced the Sm(O,F) overlayers. In this article, the T_c^{on} of a film was determined from the intersection of the two extrapolated lines: one is drawn from the normal state just above T_c, and the other is from the superconducting transition. The T_c^{end} was defined at the disappearance of resistivity.

3. Results and discussions

Fig. 1 shows the XRD patterns of pristine SmFeAsO films grown on seven substrates, CaF_2, SrF_2, BaF_2, *r*-cut Al_2O_3, $YAlO_3$, $LaAlO_3$, and MgO. All other growth parameters such as the Fe/Sm flux ratio, p_{O2}, and p_{As} were optimized for each film growth. All the films are single-phased (except for the films on SrF_2 and BaF_2, in which

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Table 1
Parameters of substrates used in this study, *r*-cut Al_2O_3, $YAlO_3$ (110), $LaAlO_3$ (001), MgO (001), CaF_2 (001), SrF_2 (001), BaF_2 (001), and SmFeAsO (bulk).

Substrate/material	Structure	Crystal system	Lattice parameter (Å)	Atomic distance at surface (Å)
r-cut Al_2O_3	corundum	rhombohedral	$a_0 = 5.128$, $\alpha = 55°20'$	3.48
$YAlO_3$ (110)	$GdFeO_3$ (pseudo-perovskite)	orthorhombic	$a_0 = 5.179$, $b_0 = 5.329$, $c_0 = 7.370$	3.715
$LaAlO_3$ (001)	pseudo-perovskite	rhombohedral	$a_0 = 5.356$, $\alpha = 60°06'$	3.790
MgO (001)	NaCl	cubic	4.212	4.212
CaF_2 (001)	CaF_2	cubic	5.463	3.863
SrF_2 (001)	CaF_2	cubic	5.800	4.101
BaF_2 (001)	CaF_2	cubic	6.200	4.384
SmFeAsO (bulk)	ZrCuSiAs	tetragonal	$a_0 \approx 3.935$–3.94, $c_0 \approx 8.50$	

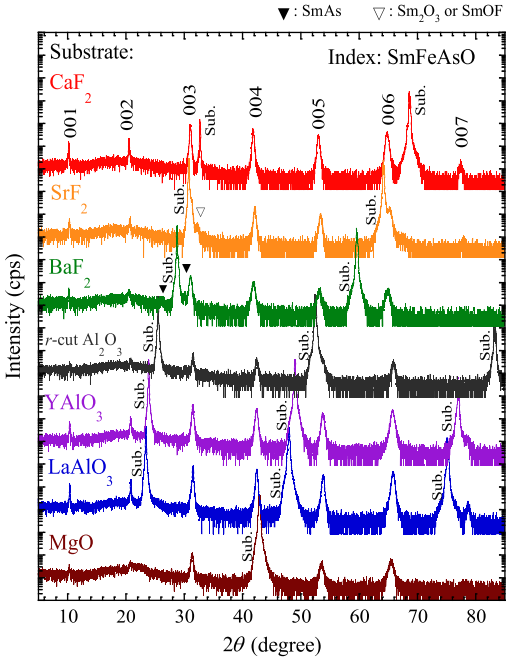

Fig. 1. XRD patterns of pristine SmFeAsO films on seven substrates.

impurity of SmAs or SmOF or Sm_2O_3 is seen) and *c*-axis oriented. The full widths at half maximum (FWHM's), $\Delta\omega$, of the ω scan (rocking curve) for the (003) reflection of the SmFeAsO films on seven substrates are summarized in Table 2 (the (004) reflection was used for the film on SrF_2 because of the overlap of the (003) reflection of the film and the (002) reflection of the substrate). Fig. 2 shows the ϕ-scan of the (102) reflection of the SmFeAsO films on CaF_2, SrF_2, BaF_2, $YAlO_3$, $LaAlO_3$, and MgO. In-plane alignment was also confirmed by the four-fold symmetry observed in four-circle X-ray diffraction measurements. The SmFeAsO film on MgO contained 45° rotated-grains, as seen in Fig. 2. The FWHM, $\Delta\phi$'s, for the (102) reflection of the SmFeAsO films are also summarized in Table 2. As can be seen in Table 2, the SmFeAsO film on CaF_2 is superior in crystalline quality to the films on the other substrates.

Table 2
Full widths at half maximum (FWHM), $\Delta\omega$, of the ω scan (rocking curve) for the (003) reflection (or for the (004) reflection of the film on SrF_2) and, $\Delta\phi$, of the ϕ scan for the (102) reflection in SmFeAsO films on various substrates.

Substrate	FWHM $\Delta\omega$ of the (003) (°)	FWHM $\Delta\phi$ of the (102) (°)
CaF_2	0.35	~0.50
SrF_2	1.0	~1.2
BaF_2	2.0	~2.2
$LaAlO_3$	0.82	~1.1
$YAlO_3$	1.0	~1.4
MgO	2.4	~3.0
r-cut Al_2O_3	4.1	–

The lattice parameters (c_0 and a_0) of these films (except for a_0 of the film on *r*-cut Al_2O_3) evaluated from the XRD measurements are summarized in Fig. 3. We can see a trend in Fig. 3 that the films on all the substrates have a slightly longer c_0 and a slightly shorter a_0 than those reported for bulk samples (c_0 (bulk) ≈ 8.50 Å and a_0 (bulk) ≈ 3.935–3.94 Å) [7,8]. Of these films, the films on CaF_2 have the longest c_0 and the shortest a_0 although there is a wide spread in c_0 and a_0. The highly crystalline films grown on CaF_2 typically have $c_0 \approx 8.62$–8.65 Å and $a_0 \approx 3.87$–3.88 Å. The a_0 value is close to the Ca–Ca distance ($a_s/\sqrt{2} = 3.863$ Å) of CaF_2 (see Table 1), suggesting that in-plane compressive epitaxial strain is introduced into the films. It is well established in the growth of oxide films that in-plane compression leads to out-of-plane expansion due to the Poisson effect [9]. Epitaxial strain tends to be relaxed in SmFeAsO films with poorer crystallinity. Hence the epitaxial strain can be controlled via crystallinity by varying the growth conditions, especially the oxygen atmosphere (O_2 flow) during growth, as we have demonstrated before [5,10]. The slight deviation of the O_2 flow from the optimum value reduces the XRD peak intensity of the *RE*-1111 phase dramatically, at the same time leading to shorter c_0.

The structural distortion on the other substrates may not be explained by simple epitaxial strain due to lattice mismatch. It is firstly because the a_0 (bulk) of SmFeAsO is far from the a_s of the substrates and secondly because SrF_2, BaF_2, and MgO yielded films with shorter a_0 and longer c_0, as seen in Fig. 3. If the structural distortion *were* due to epitaxial strain, then SrF_2, BaF_2, and MgO with a_s longer than a_0 of SmFeAsO (Table 1) *would* introduce tensile strain into a film, namely leading to longer a_0 and shorter c_0. But the observations are opposite. At present, we have no clear explanation for our observation of the substrate dependence of the film crystal structure. In this connection, it should be mentioned that Imai et al. also reported on $FeSe_{0.5}Te_{0.5}$ films grown on various substrates by pulsed laser deposition and claimed that an amorphous intermediate layer between a film and an oxide substrate plays a key role in determining the structural and superconducting properties of the grown films [11]. However, in our case, all the films except on MgO have been grown epitaxially with reasonably good crystalline quality. Hence it might be a different mechanism from Ref. [11].

Fig. 4 shows the ρ–T curves of the pristine SmFeAsO films on various substrates. The ρ–T curves of the films on oxide substrates show an anomaly at $T_N \sim 140$ K due to a magnetic transition as reported in bulk samples [7,8]. In the films on fluoride substrates, this anomaly shifts to a lower temperature (~120 K) and furthermore a superconducting transition is sometimes observed. These results suggest that F is introduced to films from fluoride substrates.

Next we present the results on F-diffused SmFeAs(O,F) films. Fig. 5 shows the XRD patterns of SmFeAs(O,F) films on seven substrates. Even if films are single phase before F diffusion, impurity phases (SmOF and $SmO_{0.7}F_{1.6}$) always appeared after F diffusion. The *RE*-1111 peaks showed a shift to a higher angle and some broadening after F diffusion, indicating that F substitutes for the O site of SmFeAsO but not very uniformly. The $\Delta\omega$ and $\Delta\phi$ also increased, for example, in films on CaF_2, from 0.35° and 0.50° to 0.81°