K-doped Ba122 epitaxial thin film on MgO substrate by buffer engineering

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Abstract

Molecular beam epitaxy of K-doped Ba122 (Ba\textsubscript{1−x}K\textsubscript{x}Fe\textsubscript{2}As\textsubscript{2}) superconductor was realized on an MgO substrate. Microstructural observation revealed that the undoped Ba122 served as a perfect buffer layer for epitaxial growth of the K-doped Ba122. The film exhibited a high critical temperature of 39.8 K and a high critical current density of 3.9 MA cm\textsuperscript{−2} at 4 K. The successful growth of epitaxial thin film will enable artificial single grain boundary on oxide bicrystal substrates and reveal the grain boundary transport nature of K-doped Ba122.

Keywords: epitaxial thin films, Ba\textsubscript{1−x}K\textsubscript{x}Fe\textsubscript{2}As\textsubscript{2}, buffer layer

(Some figures may appear in colour only in the online journal)

1. Introduction

The iron-based superconductor [1], K-doped Ba122 (Ba\textsubscript{1−x}K\textsubscript{x}Fe\textsubscript{2}As\textsubscript{2}), with a high critical temperature \(T_c = 38\) K and a high upper critical field \(\mu_0 H_{c2} \sim 100\) T, is one of the most promising materials for high-field applications [2–4]. For practical applications, it is necessary to minimize the adverse effect of the weak-link at grain boundaries, which limits transport superconducting current [5]. For the past decade, research on polycrystalline K-doped Ba122 has been conducted and demonstrated the improvement of transport critical current density (\(J_c\)) of bulks [6, 7], wires, and tapes [8, 9]. Recently, a high \(J_c\) of 1.1 × 10\textsuperscript{5} A cm\textsuperscript{−2} at 4.2 K under a magnetic field of 10 T was achieved by densification and uniaxial grain texturing [10]. For further improvement of \(J_c\), understanding the nature of grain boundaries is necessary.

The transport measurements over a single grain boundary are a clear-cut method in understanding the nature of the grain boundary. So far, in the Co- and P-doped Ba122, the transport properties across the grain boundary have been evaluated using bicrystal thin films [11, 12]. The results have both proven their advantageous grain boundary transport properties, namely lower \(J_c\) suppression with the grain boundary angle in comparison with the high-\(T_c\) cuprates [13]. Differently from Co- and P-doped Ba122, however, the volatility of K provides a serious problem in the epitaxial growth of K-doped Ba122. Recently, we have reported the successful
epitaxial growth of K-doped Ba122 by employing fluoride substrates (CaF$_2$, SrF$_2$, and BaF$_2$) [14].

The growth of K-doped Ba122 epitaxial thin films on oxide substrates is essential for bicrystal experiments. Since the discovery of the 122-type pnictide compound [2], several groups have attempted growing K-doped Ba122 epitaxial thin films on oxide substrates. Lee et al. have attempted the growth by a two-step method; room-temperature growth of undoped Ba122 and high-temperature post-annealing with K lump [15]. Ueda et al. have performed the growth by molecular-beam epitaxy (MBE) at low temperature (∼350 °C) [16]. As for the endmember KFe$_2$As$_2$ (K122), Hiramatsu et al have prepared the film by high-temperature post-annealing of K-rich K122 film [17, 18]. All three groups reported the c-axis oriented films, however, truly epitaxial (both c-axis oriented and in-plane aligned) film was only achieved in K122 [18]. In this study, we employed MgO(001) as an oxide substrate, yet it turned out that K-doped Ba122 films directly grown on MgO(001) are not epitaxially grown [14]. To realize ideal epitaxy, proper buffer layers have to be introduced in between lower MgO substrate and upper K-doped Ba122 layers. We selected undoped Ba122 as a material for the buffer layer because it is capable of high-temperature growth, has perfect lattice matching with K-doped Ba122, and is compositionally similar to K-doped Ba122.

The resultant film demonstrated a high $T_c$ of 39.8 K and a high $J_c$ of 3.9 MA cm$^{-2}$. The successful growth of epitaxial thin films on MgO substrates with a mega order of magnitude of $J_c$ is the first step toward elucidating the nature of the grain boundaries of K-doped Ba122.

2. Experimental procedure

Film growth was performed using custom-design MBE equipped with various element rate monitoring systems. The details of the deposition method are described in our previous report [14]. Briefly, all elements except for K were supplied from resistive heating of pure metal with a purity of 99.9%, 99.98%, and 99.9999% for Ba, Fe, and As, respectively. Elemental K was supplied from In-K alloy (In$_8$K$_5$) [16, 20, 21] because of the ease of controlling evaporation rate and safety issues. Electron impact emission spectrometry (EIES) and atomic absorption spectrometry (AAS) were employed for the real-time rate monitoring of various elements: EIES for Ba and Fe, and AAS for K. K-doped Ba122 was grown at 400 °C after the growth of the undoped Ba122 buffer layer at 720 °C. The amount of supplied K was almost equal to the optimum (∼0.40) or slightly lower level to obtain the highest $T_c$. The growth rate for both processes was ∼1.5 Å s$^{-1}$ and the deposition time was 2.5 min for the undoped layer and 10 min for the K-doped layer. In this study, we used MgO(001) substrates, which are commercially available in bicrystal form. K-doped Ba122 films grown on BaF$_2$-buffered MgO substrate showed almost no appreciable degradation in the atmosphere.

The crystal structure of the films was evaluated by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The cross-sectional TEM samples were prepared by focused ion beam in a SEM (Thermo Fisher Scientific Scios). The scanning-TEM (STEM, Thermo Fisher Scientific Titan G2 Cubed 60-300) was utilized for microstructural analysis equipped with bright-field (BF) and annular dark-field (ADF) detectors, and chemical compositional analysis by energy-dispersive x-ray spectroscopy (EDS). These analyses were operated at an acceleration voltage of 300 kV. The temperature dependence of in-plane resistivity was measured using a standard four-probe method. The resistivity of the film was calculated using the total thickness of the (Ba,K)122/Ba122 bilayer because the resistivity of the undoped Ba122 and K-doped Ba122 is comparable. Magnetic measurements were performed using on a rectangular slab (dimension of 1.512 mm × 2.194 mm × 80 nm and 2.091 mm × 2.540 mm × 80 nm for the temperature dependence of magnetic susceptibility and magnetic field dependence of $J_c$, respectively) a superconducting quantum interference device. The Bean critical-state model was applied to estimate $J_c$ values [22].

3. Results and discussion

Figure 1(a) shows the out-of-plane XRD pattern of K-doped Ba122 epitaxial thin film, which is deposited on the Ba122-buffered MgO substrate. Sharp (00l) ($l = 2, 4, 6, 8, 10$) peaks with no misorientation were detected in the whole angle range. The (002) peak which is around 29 ∼ 13.5° is a single peak, however, the split in the (00l) peaks appear above the (004) peak. With regard to the double peaks, the peak with higher intensity at a lower angle is considered to be the peak from the doped phase because the c-axis length is elongated with K doping in the K-doped Ba122 system. Accordingly, the separation of the peaks between the undoped Ba122 layer and the K-doped Ba122 layer enlarges at a higher angle region. The c-axis length of Ba122 and K-doped Ba122 was estimated to be 12.906 Å and 13.188 Å, respectively. It should be mentioned that the c-axis length of the K-doped Ba122 was much shorter than that of the Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ epitaxial thin films grown on CaF$_2$(001) substrate (13.380 Å) [14].

Figure 1(b) shows the in-plane XRD pattern around the (103) reflection peak. Single domain fourfold symmetry with full width at half maximum of $\Delta \phi ∼ 1.40°$ confirms that the film is in-plane aligned. In addition, the cube-on-cube epitaxial relationship between (Ba,K)122/Ba122 film and MgO substrate is confirmed. By comparing the crystallinity of the film grown on MgO substrate ($\Delta \theta_{008} = 0.66°$ and $\Delta \phi_{103} = 1.40°$) with our previously reported film grown on CaF$_2$ substrate ($\Delta \theta_{008} = 0.52°$ and $\Delta \phi_{103} = 1.39°$), it can be concluded that high crystallinity epitaxial K-doped Ba122 thin film was successfully grown on MgO substrate by introducing undoped Ba122 as a buffer layer. The $a$-axis length of K-doped Ba122 was estimated to be 3.931 Å, which is longer than that of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ epitaxial thin films grown on CaF$_2$(001) substrate (3.889 Å) [14]. The role of the Ba122 buffer layer is not clear at this stage. The possible reasons for the epitaxial growth...
Figure 1. (a) Out-of-plane XRD pattern for K-doped Ba122 epitaxial thin film grown on Ba122-buffered MgO(001) substrate. The peaks of the (00l) are split by a small difference between the K-doped Ba122 epitaxial film and the undoped Ba122 buffer layer. (b) Comparison of the in-plane XRD patterns for the (103) reflection of K-doped Ba122 and the (202) reflection of MgO substrate.

Figure 2. (a) Low magnification BF-STEM image of the K-doped Ba122 superconducting film on single-crystal MgO substrate with a buffer layer of undoped Ba122. (b), (d), and (e) show the atomic resolution ADF-STEM images corresponding to three feature regions: the low-angle grain boundary, the interface between K-doped Ba122 film and undoped Ba122 buffer layer, the interface between buffer layer and MgO substrate, respectively. (c) The select-area electron diffraction (SAED) pattern is according to the area which covers all three layers. (f) The line-scan EDS in scanning TEM mode, which shows the atomic percentages of each element in the K-doped Ba122, Ba122, and MgO layers.

are the improved lattice matching and the avoidance of direct contact between the K-doped Ba122 film and the oxygen in the oxide substrate due to the introduction of a buffer layer. In the cross-sectional BF-STEM image of the K-doped Ba122 film on MgO substrate, figure 2(a), thickness measurements were performed at several randomly selected locations.
for the Ba122 buffer layer and K-doped Ba122 layer, respectively. The statistics of the measured data yielded a thickness of 22 ± 2 nm for the Ba122 buffer layer and 80 ± 7 nm for the K-doped Ba122 layer. Columnar bright and dark contrasts in the epitaxial superconducting film suggest that the film contains many defects and columnar grain boundaries.

The detailed atomic-resolution STEM analysis of these sub-grain boundaries reveals that they are mostly low-angle grain boundaries, as shown in figure 2(b). Figures 2(d) and (e) show the atom resolution nanostructure of the interfaces between the K-doped Ba122 and the Ba122 layers, the Ba122 layer and MgO substrate, respectively. The perfect epitaxial relationship and interface between K-doped Ba122 and Ba122 buffer layer is revealed clearly in figure 2(d). From this image, the c-axis length of Ba122 and K-doped Ba122 are also estimated at 13.01 Å and 13.22 Å respectively (calibrated by \( c_{MgO} = 4.212 \) Å). The select-area electron diffraction pattern in figure 2(c) shows the epitaxial relationship between Ba122 and MgO substrate, that is \( (001)[100]-Ba122 \parallel (001)[100]-MgO \). The EDS analysis shown in figure 2(f) exhibits the changes of the chemical composition from undoped Ba122 to K-doped Ba122 mainly on barium and potassium. This result demonstrates that the interdiffusion of K is almost negligible, probably due to the low growth temperature (∼400 °C) of K-doped Ba122 films, which is consistent with the separation of the peaks observed in figure 1(a). The potassium concentration of the K-doped Ba122 film was estimated to be 36%, which is slightly lower than the optimal value of 40%.

Figure 3(a) shows the temperature dependence of resistivity of the film. The transition temperature is as high as 39.8 K with a sharp transition of \( \Delta T_\text{c} = 0.9 \) K. The observed \( T_\text{c} \) is higher by ∼3 K than \( T_\text{c} \) in K-doped Ba122 epitaxial thin films grown on fluoride substrates [14, 23]. The \( T_\text{c} \) enhancement is considered to be due to the epitaxial strain (also/or thermal expansion mismatch): \( \epsilon_0 = 3.917 \) Å for Ba\(_{0.64}\)K\(_{0.36}\)Fe\(_2\)As\(_2\) [24], 3.863 Å for CaF\(_2\), and 4.212 Å for MgO. The longer \( \epsilon_0 \) of MgO should introduce in-plane tensile and out-of-plane compressive strain. Normal-state resistivity at room temperature was 346 \( \mu \Omega \) cm, which should be compared with the values of single crystal (∼310 \( \mu \Omega \) cm) [25] and polycrystalline bulk (∼480 \( \mu \Omega \) cm) [26]. Residual resistivity ratio (RRR) of 5.8 was smaller than that of single crystal (∼11.6) and polycrystalline bulk (∼6.8).

Generally, RRR increases with the improved crystallinity and reduced impurity concentration. In addition, RRR varies with K content and strain induced by external pressure. Possible reasons for the relatively small RRR are an electric conductivity carried in parallel by the undoped Ba122 buffer layer, low-angle grain boundaries, and epitaxial strain.

Figure 3(b) shows the temperature dependence of normalized magnetic susceptibility for the K-doped Ba122 epitaxial thin film on Ba122-buffered MgO substrate. Inset shows the temperature dependence of resistivity near \( T_\text{c} \). (b) Temperature dependence of normalized magnetic susceptibility for the K-doped Ba122 epitaxial thin films grown on Ba122-buffered MgO substrate for the ZFC and FC process.

Figure 4 shows the magnetic field dependence of \( J_\text{c} \) at different temperatures when a magnetic field is applied parallel to the c-axis direction for the K-doped Ba122 film grown on Ba122-buffered MgO. A reasonably high self-field \( J_\text{c} \) of 3.9 MA cm\(^{-2}\) was obtained at 4 K, exceeding the values reported for K-doped Ba122 single crystals [27–29]. The \( J_\text{c}(H) \) behavior of the film at 16 K is comparable to that of the film grown on CaF\(_2\)(001) substrate at 4 K (black dashed line in figure 4). In comparison to the highest \( J_\text{c} \) reported in Co-doped Ba122 epitaxial thin film (5.6 MA cm\(^{-2}\)) [30], the \( J_\text{c} \) value is lower in self-field, but higher above 4 T. It is noteworthy...
that the $J_c$ value exceeds 1 MA cm$^{-2}$ under a high field of 7 T suggesting that the film has outstanding characteristics in magnetic fields.

4. Conclusion

In this study, we demonstrated the first successful epitaxial growth of K-doped Ba122 thin film on oxide substrate by employing undoped Ba122 as a buffer layer. The epitaxial growth was confirmed from both XRD and TEM observation. A high $T_c$ of 39.8 K exceeding the bulk value has been achieved, which is possibly due to epitaxial strain (and/or thermal expansion mismatch). A reasonably high self-field $J_s$ of 3.9 MA cm$^{-2}$ with $J_s > 1$ MA cm$^{-2}$ under a magnetic field of 7 T confirmed superior magnetic field dependence of K-doped Ba122.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Figure 4. Magnetic field dependence of critical current density measured at different temperatures. The black dashed line is the 4 K $J_c(\mu_0H)$ curve for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$/CaF$_2$ (001) [14].
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