Growth of a smooth CaF_2 layer on NdFeAsO thin film

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Abstract. We studied the method to grow a smooth and flat CaF_2 layer on NdFeAsO thin films since CaF_2 is a promising candidate material for the barrier layer of a superconducting junction. When the CaF_2 layer was grown at 800°C, the surface was very rough because {111} facets had grown preferentially. However, when CaF_2 was grown at lower temperatures and post-annealed *in situ* at 800°C for 30 min the facets were eliminated and a CaF_2 layer with a smooth surface was obtained. Fluorine diffusing from CaF_2 into NdFeAsO was observed when CaF_2 was grown at high temperatures, but the diffusion was suppressed by lowering the growth temperature to 400°C.

1. Introduction

The recently discovered iron based superconductors [1] have a high transition temperature (T_c) that benefits greatly to practical applications. Fabrication of Josephson junctions using iron-based superconductors are currently actively studied as it forms the basis of electronic applications [2]. Among the various types of junctions, sandwich-type planar junctions have an advantage of the easiness of integration, and are the most fundamental and elemental type of junctions for superconducting electronics. Fabrication of this type of junctions has been reported for $Ba(Fe,Co)_2As_2$ [3, 4], which is one of the most studied iron-based superconductors. However, a junction of this type using a *Ln*FeAs(O,F) (*Ln*=lanthanide) thin film has yet not been realized, although it has the highest T_c among the iron-based superconductors discovered so-far [5].

Over the past few years, a considerable effort has been devoted to grow high quality *Ln*FeAs(O,F) thin films. Our group has grown NdFeAs(O,F) [6-9] and LaFeAs(O,F) [10] thin films by molecular beam epitaxy (MBE). Other groups have reported on the growth of SmFeAs(O,F) thin films with a similar method [11], and LaFeAs(O,F) thin films by pulsed laser deposition [12]. As the next step toward realizing Josephson junctions, it is necessary to grow a thin and smooth barrier layer on these superconductors. CaF_2 is known as a good insulator with a wide band gap. In addition, the NdFeAs(O,F) thin film exhibited the highest T_c when it was grown on a CaF_2 substrate in our previous study where various substrates were used [9]. Therefore, the second superconducting layer that would be grown on the barrier layer is expected to have a high T_c if CaF_2 were used as the insulator.

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For these reasons, we have grown CaF_2 on NdFeAsO thin films in this work. However, as will be shown below, we found that the surface of the CaF_2 layer was very rough because {111} facets had grown preferentially. The surface roughness was too large that the fabrication of a Josephson junction would be difficult. On the other hand, it has been reported that CaF_2 layers grown on Si(100) substrates had similarly rough surfaces, but could be flattened by post-growth annealing at high temperatures [13]. This idea was applied in the present work to study the method of fabricating a flat CaF_2 layer on NdFeAsO thin film.

2. Experiment

NdFeAsO thin films with a thickness of 50 nm were grown on MgO(100) substrates by MBE. The growth method was similar to that reported elsewhere [8], except that the growth temperature was increased to 800ºC and the oxygen source was changed to He diluted O_2 gas. In the present study, we focused on fabricating a flat and smooth CaF_2 layer on the NdFeAsO phase. Therefore, fluorine was not doped to the NdFeAsO phase to shorten the fabrication process. After the growth of the NdFeAsO layer, CaF_2 was grown with a rate of 5 nm/min for 5 min at temperatures that will be described later. A Knudsen cell was used to supply CaF_2. After the growth of CaF_2, some of the thin films were annealed at 800ºC for 30 min, which was carried out *in situ*.

Reflection high energy electron diffraction (RHEED) was used to characterize the surface during thin film growth. The obtained thin films were characterized by x-ray diffraction (XRD), atomic force microscope (AFM), and transmission electron microscope (TEM), and the composition by electron probe microanalysis (EPMA). Resistivity was measured by a four-probe method.

3. Results

Figure 1(a) shows an AFM image of CaF_2 grown at 800°C on NdFeAsO. Obviously, the surface is very rough and consists of many islands. The root mean square roughness (R_{RMS}) was 17.8 nm, which is too large for junction fabrication. Figure 1(b) shows the RHEED pattern after the growth of CaF_2 for the same sample. While a streaky RHEED pattern was observed during the growth of NdFeAsO that indicates the base layer was flat, the RHEED pattern of the CaF_2 layer was spotty, consistent with the island structures shown in figure 1(a). Weak streaks running between the spots can also be seen in figure 1(b). The angle between the off-angle streaks is 109°, which indicates the existence of {111} facets.

The formation of a faceted surface was also reported when CaF_2 was grown on Si(100) substrates [13,14]. In addition, it was shown that the CaF_2 surface can be flattened by post-growth annealing [13]. Figure 2 shows AFM images of two CaF_2 layers grown on NdFeAsO at 800 and 600°C, both followed by an annealing at 800°C for 30 min. When the growth temperature (T_g) was 800°C, the CaF_2 surface had a morphology similar to figure 1(a), thus the annealing had no effect on the surface roughness. On the other hand, the T_g = 600°C sample had a far smoother surface. Figure 3 indicates the RHEED patterns of the sample shown in figure 2(b). Figure 3(a) was taken right after the growth of CaF_2, which was spotty and indicates an island growth mode. The RHEED pattern changed to a streaky one after annealing as shown in figure 3(b). Thus, the flattening of the surface occurred during the annealing at 800°C.

We have also grown the CaF_2 layer at a lower temperature, T_g = 400°C, and annealed it at 800°C. Figure 4(a) shows the AFM image of this sample. R_{RMS} was 2.38 nm, which is better than the T_g = 600°C sample. Figures 4(b) and (c) show cross-sectional scanning TEM (STEM) images of the T_g = 800°C (figure 2(a)) and T_g = 400°C (figure 4(a)) samples. Consistent with the AFM images, the

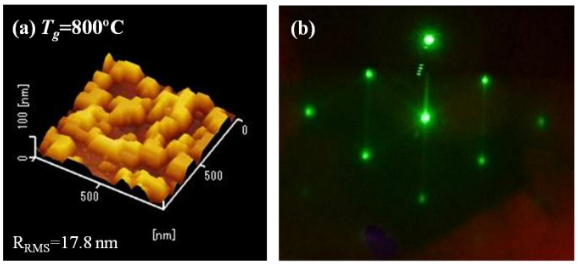

Figure 1. (a) An AFM image of the CaF_2 layer grown at 800ºC on NdFeAsO. (b) The RHEED image of the same sample right after the growth of CaF_2.

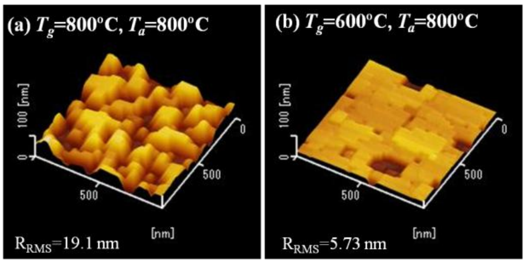

Figure 2. AFM images of the CaF_2 layers grown on NdFeAsO at (a) 800ºC and (b) 600ºC. Both samples were annealed at 800ºC for 30 min.

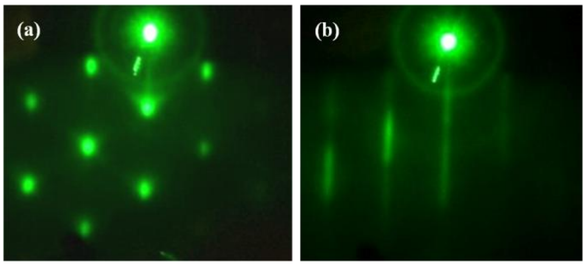

Figure 3. RHEED patterns of the same sample as figure 2(b) taken (a) before and (b) after annealing at 800ºC for 30 min.

STEM observation revealed a very rough surface for the T_g = 800°C sample. It should also be noted that NdFeAsO is covered only partially with CaF_2. In contrast, CaF_2 covered completely NdFeAsO when it was grown at 400°C.

4. Discussion

The faceted growth of CaF_2 can be understood by the difference in the free energies of the {111} and {100} surfaces [14]. As mentioned above, Asano *et al*. have shown that a flat CaF_2 layer can be obtained on Si(100) by post-annealing [13]. They have also grown a second CaF_2 layer on the post-annealed (flattened) first layer, and found that the surface was facetted again when the second layer was grown at 600°C but remained flat at 800°C, which led them to suggest that the relative ratio of the free energy might alter at high temperatures. This is consistent with the RHEED patterns shown in figure 3 that suggest the {111} plane of CaF_2 is stable at 600°C while the {100} plane is more stable at 800°C. However, in contrast to the second CaF_2 layer on the flattened first layer in the study by Asano *et al*., our sample had a rough surface when CaF_2 was grown at 800°C (figure 2(a)). A possible reason might be that the bonding between CaF_2 is stronger than that to NdFeAsO. In that case, island growth of CaF_2 can take place before the NdFeAsO surface is covered if the migration of CaF_2 is sufficiently large at high temperatures. This is probably the reason why part of the surface of NdFeAsO was not covered in figure 4(b). At lower temperatures, on the other hand, CaF_2 covers the surface of NdFeAsO (figure 4(c)) because the migration is suppressed.

Figure 5 shows the temperature (T) dependence of resistivity (ρ) of the thin films prepared with different growth temperatures of CaF_2. As mentioned above, we used non-doped NdFeAsO as the base layer, and a superconducting transition was not expected. However, we observed clear superconducting transitions for the T_g = 600 and 800°C thin films, which suggest that fluorine had diffused from CaF_2 to the NdFeAsO layer. The lower T_c of the T_g = 600°C thin film, together with the behavior of the ρ-T curve, indicates that this film has a lower fluorine content. On the other hand, no superconducting transition was observed for the T_g = 400°C thin film. Hence, the higher the growth temperature, the more fluorine was diffused into the NdFeAsO layer. Note that all three samples were

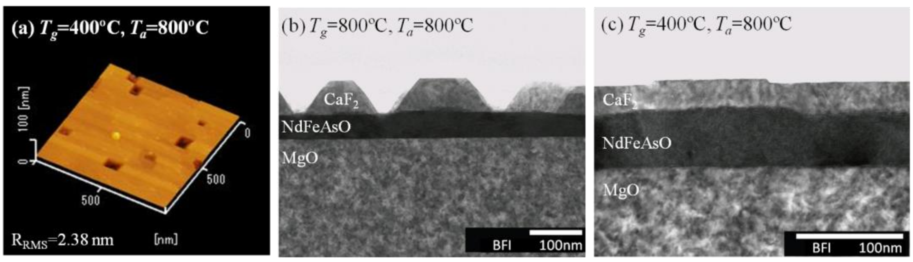

Figure 4. (a) An AFM image of the CaF_2 layer grown on NdFeAsO at 400ºC and annealed at 800ºC. (b) A cross-sectional STEM image of the sample shown in figure 2(a). (c) A cross-sectional STEM image of the sample shown in figure 4(a).

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annealed at 800°C for 30 min after the growth of CaF_2, which is equal to the highest T_g of the three samples. Nevertheless, the amount of diffused fluorine depended on the growth temperature, suggesting that fluorine diffusion did not occur during annealing but the growth process. We speculate that fluorine may easily diffuse from molecular CaF_2 at the arrival at the substrate when it has enough thermal energy, but not after it is crystallized. Regardless of the reason why fluorine diffusion depended on T_g, however, the results of figure 5 suggest that fluorine was not diffused from CaF_2 into the NdFeAsO phase for the T_g = 400°C thin film and we can expect that a good interface is formed between the two layers.

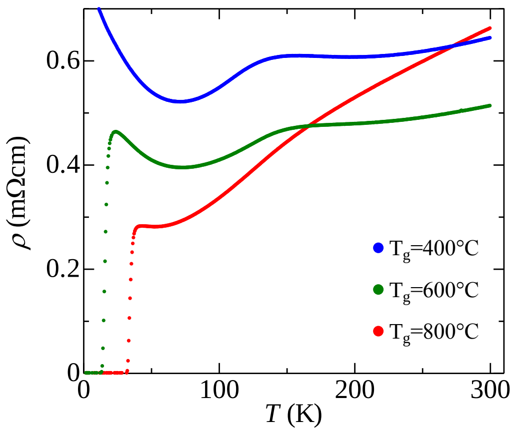

Figure 5. Temperature dependence of resistivity of CaF_2/NdFeAsO/MgO multilayers. CaF_2 was grown at 400, 600 and 800ºC, all followed by an annealing at 800ºC for 30 min.

5. Conclusions

Aiming the fabrication of sandwich-type planar superconducting junctions, we studied the method to fabricate a flat and smooth CaF_2 layer on NdFeAsO thin films. The as-grown CaF_2 layer exhibited a very rough and faceted surface. The facets were eliminated and a flat surface was obtained by post-growth annealing at 800°C when CaF_2 was grown at lower temperatures. Fluorine diffusing from CaF_2 into NdFeAsO was observed when CaF_2 was grown at high temperatures, but was suppressed at T_g = 400°C.

Acknowledgements

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References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296
[2] Seidel P 2011 *Supercond. Sci. Technol.* **24** 043001
[3] Schmidt S, Döring S, Schmidl F, Grosse V, Seidel P, Iida K, Kurth F, Haindl S, Mönch I and Holzapfel B 2010 *Appl. Phys. Lett.* **97** 172504
[4] Döring S, Schmidt S, Schmidl F, Tympel V, Haindl S, Kurth F, Iida K, Mönch I, Holzapfel B and Seidel P 2012 *Physica C* **478** 15
[5] Tanabe K and Hosono H 2012 *Jpn. J. Appl. Phys.* **51** 010005
[6] Kawaguchi T, Uemura H, Ohno T, Watanabe R, Tabuchi M, Ujihara T, Takeda Y and Ikuta H 2009 *Appl. Phys. Express* **2** 093002
[7] Kawaguchi T, Uemura H, Ohno T, Tabuchi M, Ujihara T, K. Takenaka, Takeda Y and Ikuta H 2010 Appl. Phys. Lett. **97** 042509
[8] Kawaguchi T, Uemura H, Ohno T, Tabuchi M, Ujihara T, Takeda Y and Ikuta H 2011 *Appl. Phys. Express* **4** 083102
[9] Uemura H, Kawaguchi T, Ohno T, Tabuchi M, Ujihara T, Takeda Y and Ikuta H 2012 *Solid State Commun.* **152** 735
[10] Kawaguchi T, Uemura H, Ohno T, Tabuchi M, Ujihara T, K. Takenaka, Takeda Y and Ikuta H 2011 *Physica C* **471** 1174
[11] Ueda S, Takeda S, Takano S, Yamamoto A and Naito M 2011 *Appl. Phys. Lett.* **99** 232505
[12] Kidszun M, Haindl S, Reich E, Hänisch J, Iida K, Schultz L and Holzapfel B 2010 *Supercond. Sci. Technol.* **23** 022002
[13] Asano T, Ishiwara H and Furukawa S 1988 *Jpn. J. Appl. Phys.* **27** 1193
[14] Fathauer R W and Schowalter L J 1984 *Appl. Phys. Lett.* **45** 519