Direct growth of superconducting NdFeAs(O,F) thin films by MBE

Masashi Chihara¹, Naoki Sumiya¹, Kenta Arai¹, Ataru Ichinose², Ichiro Tsukada², Takafumi Hatano¹, Kazumasa Iida¹, Hiroshi Ikuta¹

¹Department of Crystalline Materials Science, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

²Central Research Institute of Electric Power Industry, Yokosuka-shi, Kanagawa 240-0101, Japan

Phone number: +81 52 789 3822.

E-mail address: chihara@iku.xtal.nagoya-u.ac.jp (M. Chihara)

Postal address: Department of Crystalline Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 463-8603, Japan

Abstract

We report on the growth of NdFeAs(O,F) superconducting thin films by molecular beam epitaxy without having a NdOF secondary layer that was necessary for fluorine doping in our previous studies. The key to realizing the direct growth of a superconducting film was the enhancement of migration of the raw materials on the substrate, which was accomplished by two steps. Firstly, we increased the growth temperature that improved the crystalline quality of parent NdFeAsO thin films. Secondly, the atmosphere in the chamber during the growth was improved by changing the crucible material of the Fe source cell. Highly textured NdFeAs(O,F) thin films with critical temperatures up to 50 K were obtained, and terraces were observed by atomic force microscope, indicating a two-dimensional growth. However, precipitates were also found on the surface, which suggests that enhancing further the migration is necessary for obtaining a NdFeAs(O,F) thin film with a better quality.

Keywords: Molecular beam epitaxy, Iron-based superconductor, *Ln*FeAs(O,F), Epitaxial thin film, Oxypnictide

1. Introduction

Among the various iron-based superconductors discovered to date, *Ln*FeAs(O,F) (*Ln*: lanthanoid, hereafter 1111) has the highest critical temperature (T_c) that is a great advantage for applications [1]. The growth of 1111 thin films started therefore right after the discovery of these compounds. However, this material contains volatile elements such as oxygen, fluorine and arsenic that makes the crystal growth very difficult. Hiramatsu *et al.* have reported on the first successful growth of epitaxial LaFeAsO thin films by pulsed laser deposition (PLD). However, the films did not show any sign of superconductivity due to the lack of fluorine [2]. At almost the same time, the preparation of LaFeAs(O,F) thin films was reported by another group, who, however, had to combine an *ex-situ* thermal treatment to PLD to obtain superconducting thin films [3-5]. On the other hand, our group has succeeded in *in-situ* growth of superconducting NdFeAs(O,F) thin films on various substrates with T_c up to 56 K by molecular beam epitaxy (MBE) [6-9]. In our process, however, it was necessary to grow NdOF on a NdFeAsO parent phase layer, so that fluorine diffused into the 1111 phase from the top fluoride layer. A similar method was also applied to SmFeAs(O,F) by Ueda *et al.* [10].

Hence, although they readily yield 1111 thin films with high T_c , the aforementioned processes adopt either an *ex-situ* process or a fluorine reservoir layer to obtain a superconducting thin film. These methods are obviously unfavorable for some applications, such as *in-situ* fabrication of stack-type superconducting devices. Therefore, there is a great demand for a direct growth method of superconducting 1111 thin films. Quite recently, Sugawara *et al.* reported that direct growth of SmFeAs(O,F) was possible by using FeF₂ as the fluorine source [11]. On the other hand, we report here that direct growth of superconducting 1111 thin films is possible with yet another method. We investigated our growth process thoroughly, and identified the fundamental problem for the incomplete growth of NdFeAs(O,F) films as an insufficient migration of raw materials on the substrate. We propose two methods in order to enhance the migration rate. Firstly, the growth temperature was increased, which directly enhanced the migration rate. Secondly, we found that there existed a large amount of unnecessary N₂ gas during the growth, which was largely suppressed by changing the crucible material of the Fe cell. By a combination of these two attempts, direct growth of NdFeAs(O,F) superconducting thin films was realized.

2. Experimental details

NdFeAs(O,F) thin films with a thickness of 30 nm were grown on MgO (001) substrates at a rate of 1 nm/min by MBE. Solid sources of Fe, As, NdF₃, and Ga were charged in Knudsen cells. Here, Ga was used as a F-getter to control the amount of fluorine [8]. Oxygen was supplied by a compressed O₂ gas cylinder diluted with He by 20 times. The vapor pressures of NdF₃, Fe, and Ga were of the order of 10⁻⁶ Pa, As was of the order of 10⁻³ Pa, while the gas pressure of He + O₂ was of the order of 10⁻⁴ Pa. The heating system was modified from our previous studies to make it possible to increase the substrate temperature, which was varied from 600 to 800°C in this study. Partial pressures in the growth chamber were measured by a quadrupole mass spectrometer (QMS). [Reflection high energy electron diffraction \(RHEED\)](#) was used for *in-situ* monitoring the surface structure during the thin film growth. Phase purity and crystalline quality of the obtained thin films were examined by x-ray diffraction (XRD) using a Cu-K α radiation. Surface

morphology of the films was observed by an atomic force microscope (AFM). Microstructural analyses have been performed by using transmission electron microscope (TEM) equipped with an energy dispersive x-ray spectrometer. Resistivity was measured with a four-probe method. A micro-bridge with a width of 10 μm fabricated through a photolithography process, followed by ion-beam etching was used for in-field critical current density (J_c) measurements. A voltage criterion of 1 μV was employed for evaluating J_c .

3. Results and discussion

Figure 1(a) shows the XRD patterns of parent phase NdFeAsO thin films grown at 600-800°C. (00 l)-oriented and phase pure NdFeAsO films were obtained at various substrate temperatures by optimizing the growth conditions. As can be seen in Fig. 1(a), the intensities of the (00 l) peaks of NdFeAsO increased with increasing the growth temperature. Figure 1(b) shows the growth temperature dependence of full width at half maximum (FWHM, $\Delta\omega$) of the (003) rocking curve for the NdFeAsO films. Clearly, the film quality improved substantially by increasing the growth temperature to 750°C or higher and $\Delta\omega$ was very small, less than 0.5°.

As the next step, we tried to grow fluorine-doped NdFeAs(O,F) thin films at 800°C by adjusting the supply of O₂ and Ga starting from the **undoped** film shown in Fig. 1(a). However, these thin films did not show any sign of superconductivity until the lowest temperature available in our resistivity measurement system. Hence, even with the high growth temperature of 800°C, it seems that migration was still insufficient. In order to identify the origin of low migrations, we measured the partial pressure inside the chamber during the film growth using QMS. As a result, a significant amount of N₂ of the order of 10⁻⁵ Pa was detected, which was about one-tenth of the chamber pressure during the growth. In addition, the partial pressure of N₂ notably increased with heating the Fe-cell, which indicates the pyrolytic boron nitride (pBN) crucible we were using may have reacted with Fe. Because this huge amount of N₂ is a possible source to reduce the migration, we changed the pBN crucible to an Al₂O₃ one, and the amount of N₂ was greatly suppressed to the order of 10⁻⁸ Pa even with heating the Fe source.

After this second improvement, NdFeAs(O,F) thin films were prepared at 800°C. Figure 2 summarizes the results of thin film growth by systematically changing O₂ and Ga fluxes. Note here that a decrease in Ga flux leads to an increase in F supply. With increasing the Ga flux, no F was incorporated to the thin film and parent phase NdFeAsO with/without impurities in XRD was obtained (blue triangle/circle). By contrast, only impurity phases were observed **irrespective of the O₂ flux when the Ga flux was low** (cross) because of the excess amount of fluorine. On the other hand, despite the narrow growth window as indicated by red circle and triangles, superconducting NdFeAs(O,F) thin films have been realized by adjusting O₂ and Ga partial pressures appropriately (see Fig. 3). Figure 3 shows XRD pattern and temperature dependence of resistivity of the NdFeAs(O,F) thin film that corresponds to the red circle in Fig. 2. **The (00 l) peaks of this film were weaker compared with those of the parent phase NdFeAsO thin film grown at the same temperature (800°C), but almost as sharp as those of the parent phase film.** As can be seen in Fig. 3, this thin film showed a clear superconducting transition, although the onset transition temperature was 37 K, indicating that there is still room for improving T_c .

Further optimizing the conditions at 750 and 800°C yielded four phase-pure NdFeAs(O,F) thin films. The representative results of XRD and resistivity are shown in Fig. 4. **The four-fold symmetry with an average FWHM value of $\Delta\phi = 1.27^\circ$ is revealed in the inset, indicative of epitaxial growth.** Furthermore, the (003) rocking curve measurement showed $\Delta\omega = 0.77^\circ$. These results prove that the 1111 phase had a high crystalline quality. The temperature dependence of resistivity is shown in Fig. 4(b). It is worth mentioning that an onset T_c of 50 K is relatively high for NdFeAs(O,F) thin films grown on MgO substrates [9]. Without intentional introduction of flux pinning, our film showed a high J_c performance as well, as shown in Fig. 5. The data was acquired at 4 K for magnetic field parallel to the c -axis. As can be seen from Fig. 5, the self-field J_c exceeded 3 MA/cm². Even in the presence of magnetic field of 9 T, J_c maintained 1 MA/cm², which is the highest J_c reported for 1111 thin films so far [12]. The high J_c of our thin film is a proof that the superconductivity has a bulk nature and is not governed by a region that was accidentally fluoridized.

Shown in Fig. 6(a) is the surface morphology of the superconducting NdFeAs(O,F) thin film presented in Fig. 4. It is clear that several precipitates were observed at the surface, but despite the presence of such precipitates, several terraces were observed. Figure 6(b) plots line profiles along the red and blue lines of Fig. 6(a) that reveal step heights of about 0.9 nm, which corresponds to the c -axis lattice constant of 1111. These results indicate the two-dimensional growth of the 1111 phase. **The RHEED pattern of this sample was streaky until the end of the growth, but was spotty after the substrate was cooled to room temperature.**

Figure 7(a) shows a cross-sectional scanning TEM (STEM) image around the interface between NdFeAs(O,F) thin film and MgO substrate. For the TEM observation, we used the sample presented in Fig. 3. The STEM image revealed a clean interface without appreciable defects in the NdFeAs(O,F) matrix. However, non-1111 phase region that has a light contrast was clearly seen at the surface in some part of the thin film (Fig. 7(b)). Elemental mapping shown in Fig. 7(c) revealed that this non-1111 phase contained mainly neodymium and oxygen, since the intensities of As, F and Fe are relatively low compared to the NdFeAs(O,F) region. Hence this non-1111 phase is probably a NdO-rich compound. **The RHEED pattern of this thin film was streaky at the beginning, but became a mixture of spotty and streaked pattern after about half the growth time, suggesting that the rather large impurity observed in the middle of Fig. 7(b) was formed during the growth.** This is different from the growth of the sample used for AFM observation of Fig. 6, for which the RHEED pattern was streaky until the end of the growth. However, there is a smaller region near the surface in Fig. 7(b)

(upper right) that is also deficient in As, F, and Fe. We think that the precipitates observed by AFM correspond to these NdO-rich compound formed at the surface.

Previously we have attempted direct growth of NdFeAs(O,F) but no superconducting phase was obtained [8]. Therefore, we conclude that the enhancement of migration that was accomplished in the present study was crucial to realize direct growth of superconducting thin films. However, there seems to be still some uncontrollable factors in the growth. Indeed, non-1111 phase, which was undetectable in XRD, were observed in Fig. 6 and 7. Additionally, five phase-pure superconducting thin films have been obtained so far, but T_c of those thin films varied. We think that these problems indicate that migration of the raw materials is still insufficient and has to be further optimized by, for instance, re-considering the raw materials to obtain superconducting thin films with a better reproducibility.

4. Summary

In conclusion, superconducting NdFeAs(O,F) thin films were obtained by a direct growth method. The key to achieving this result was enhancing the migration of the raw materials on the substrate by increasing the growth temperature and suppressing the unwanted N_2 gas during the film growth. Highly textured NdFeAs(O,F) thin films with critical temperatures up to 50 K have been obtained, and terraces were observed in atomic force microscope observations, indicative of a two-dimensional growth. However, precipitates were also observed on the surface, which suggests that a yet more enhancement of migration is necessary to obtain NdFeAs(O,F) thin films with further improved quality and better controllability.

Acknowledgements

This study was partially supported by Strategic International Collaborative Research Program (SICORP), Japan Science and Technology Agency, and by a Grant-in-Aid from MEXT, Japan.

References

- [1] for a review, see for instance K. Tanabe and H. Hosono, Jpn. J. Appl. Phys. **51** (2012) 010005.
- [2] H. Hiramatsu, T. Katase, T. Kamiya, M. Hirano, H. Hosono, Appl. Phys. Lett. **93** (2008) 162504.
- [3] E. Backen, S. Haindl, T. Niemeier, R. Hühne, T. Freudenberg, J. Werner, G. Behr, L. Schultz, B. Holzapfel, Supercond. Sci. Technol. **21** (2008) 122001.
- [4] M. Kidszun, S. Haindl, E. Reich, J. Hänisch, K. Iida, L. Schultz, B. Holzapfel, Supercond. Sci. Technol. **23** (2010) 022002.
- [5] M. Kidszun, S. Haindl, T. Thersleff, J. Werner, M. Langer, J. Hänisch, K. Iida, E. Reich, L. Schultz, B. Holzapfel, Europhys. Lett. **90** (2010) 57005.
- [6] T. Kawaguchi, H. Uemura, T. Ohno, R. Watanabe, M. Tabuchi, T. Ujihara, K. Takenaka, Y. Takeda, H. Ikuta, Appl. Phys. Express **2** (2009) 093002.
- [7] T. Kawaguchi, H. Uemura, T. Ohno, M. Tabuchi, T. Ujihara, K. Takenaka, Y. Takeda, H. Ikuta, Appl. Phys. Lett. **97** (2010) 042509.
- [8] T. Kawaguchi, H. Uemura, T. Ohno, M. Tabuchi, T. Ujihara, Y. Takeda, H. Ikuta, Appl. Phys. Express **4** (2011) 083102.
- [9] H. Uemura, T. Kawaguchi, T. Ohno, M. Tabuchi, T. Ujihara, Y. Takeda, H. Ikuta, Solid State Commun. **152** (2012) 735.
- [10] S. Ueda, S. Takeda, S. Takano, A. Yamamoto, M. Naito, Appl. Phys. Lett. **99** (2011) 232505.
- [11] H. Sugawara, T. Tsuneki, D. Watanabe, A. Yamamoto, M. Sakoda, M. Naito, Supercond. Sci. Technol. **28** (2015) 015005.
- [12] K. Iida, J. Hänisch, C. Tarantini, F. Kurth, J. Jaroszynski, S. Ueda, M. Naito, A. Ichinose, I. Tsukada, E. Reich, V. Grinenko, L. Schultz, B. Holzapfel, Sci. Rep. **3** (2013) 2139.

Figure captions

- Fig. 1. (a) XRD patterns of parent phase NdFeAsO thin films grown at various growth temperatures. (b) FWHM of the (003) rocking curve as a function of growth temperature.
- Fig. 2. Summary of the results of thin film growth at various O_2 and Ga fluxes at 800°C. All the other growth parameters were the same for these thin films.
- Fig. 3. XRD pattern of a directly grown NdFeAs(O,F) thin film that corresponds to the red circle in Fig. 2. The inset shows temperature dependence of resistivity of the same thin film.
- Fig. 4. (a) XRD pattern and (b) temperature dependence of resistivity of a directly grown NdFeAs(O,F) thin film after adjusting the various growth conditions. The inset to (a) shows the result of (200) peak ϕ -scan measurement of the same thin film.
- Fig. 5. Critical current density J_c as a function of magnetic field up to 9 T at 4 K for the thin film shown in Fig. 4.
- Fig. 6. (a) Surface morphology observed by AFM of the thin film shown in Fig. 4. (b) Height profiles along the red (upper panel) and blue (lower panel) lines shown in (a).
- Fig. 7. (a) Cross-sectional scanning TEM image around the interface between the substrate and NdFeAs(O,F) of the thin film shown in Fig. 3, (b) cross-sectional scanning TEM image with a low magnification and (c) its elemental mapping measurements.

Figure 1

Figure 8

Figure''

Figure (

Figure')

Figure*

Figure +