In situ growth of superconducting NdFeAs(O,F) thin films by molecular beam epitaxy

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Superconducting NdFeAs(O,F) thin films were grown on GaAs substrates by molecular beam epitaxy. Films grown with a sufficiently long growth time exhibited a clear superconducting transition with an onset temperature up to 48 K and zero resistance temperature up to 42 K without the need of an *ex situ* annealing process. Electron probe microanalysis and Hall coefficient measurements indicated that the superconducting films are doped with fluorine, and depth-profile analysis by Auger electron spectroscopy revealed the formation of a NdOF layer near the surface, which is probably connected with the fluorine doping. © *2010 American Institute of Physics*. [doi:10.1063/1.3464171]

The recently discovered high temperature superconductor F-doped LaFeAsO (Ref. 1) and related compounds[2–8] represent a class of superconductors with the highest transition temperature (T_c) apart from the cuprates. The studies ongoing worldwide are revealing that these Fe-based superconductors are forming a unique class of materials that are interesting from the viewpoint of applications. To exploit the high potential of the Fe-based superconductors for device applications, it is indispensable to establish a process that enables the growth of high quality thin films. Studies on thin film preparation started soon after the discovery of Fe-based superconductors,[9–11] and many research groups have been reporting on thin films of Co-doped $AE\mathrm{Fe_2As_2}$ (AE=Sr,Ba) (Refs. 10, 12, and 13) and iron-chalcogens,[14–16] the best films of which already possessing a T_c value exceeding 20 K. Quite recently, the fabrication of K-doped $\mathrm{BaFe_2As_2}$ with an onset T_c up to 40 K was also reported.[17]

In contrast, growing thin films of *Ln*FeAsO (*Ln*=lanthanide), the so-called 1111 family, which possesses the highest T_c of 56 K among the Fe-based superconductors known to date, has been confronted with more difficulties. Hiramatsu *et al.*[9] prepared La-1111 films by pulsed-laser deposition (PLD) on oxide crystalline substrates. They have succeeded in obtaining epitaxial films but the films did not show a superconducting transition. Soon thereafter, another group had succeeded in the preparation of F-doped La-1111 thin films that exhibited superconducting transitions.[11,18] However, it was necessary to treat these films *ex situ* at significantly high temperatures to form the 1111 phase. The necessity of such heat treatment places a considerable burden on the processing of superconducting devices, and the development of a procedure that does not require a subsequent high-temperature treatment is a necessary next step.

While the above mentioned two groups had employed PLD methods, we have succeeded in growing Nd-1111 thin films by molecular beam epitaxy (MBE) in a previous work.[19] The films were grown on GaAs substrates, which also differentiates our work from the other studies. GaAs was selected because of its good lattice matching with *Ln*-1111 and the similarity in the atomic coordination around As. We also expect that various growth techniques established in studies on semiconductors, such as strain control by an alloy buffer layer, can be applied when GaAs is used as a substrate, and interesting devices may be realized by combining a superconductor with a semiconductor.

The growth condition for obtaining a single-phased film of Nd-1111 with a very high reproducibility was identified from a detailed study in our previous work.[19] However, the film did not show a superconducting transition and the resistivity increased at low temperature. Because that film was only 15 nm thick, we speculated that it might have some structural imperfections. Therefore, the effect of increasing the film thickness was studied in the present work. As a result, we succeeded in obtaining as-grown, superconducting thin films of F-doped Nd-1111. The highest onset temperature T_c^{onset} of these films was 48 K with a zero resistance temperature T_c^0 of 42 K. This was achieved without an *ex situ* heat treatment, and the observed T_c is the highest among the so-far reported thin films of Fe-based superconductors.

The thin films were grown by a MBE method, the detail of which is reported in the previous paper.[19] Briefly, GaAs(001) was used as substrates, on which an about 300 nm thick GaAs buffer layer was grown at 610 °C after the oxide layer on the substrate was removed by sublimation. Nd-1111 was grown by supplying all elements from solid sources charged in Knudsen cells; Fe, As, $\mathrm{NdF_3}$, and $\mathrm{Fe_2O_3}$. The substrate temperature was 650 °C and the vapor pressures of Fe, As, $\mathrm{NdF_3}$, and oxygen were 1.9×10^{-6} Pa, 1.5×10^{-3} Pa, 2.7×10^{-6} Pa, and 2×10^{-5} Pa, respectively. The composition of the films was checked by electron probe microanalysis (EPMA) using Nd-1111 powders as a reference. Depth-profile analysis was performed using an Auger electron spectroscopy combined with Ar ion sputtering (JEOL JAMP-7800). The growth rate of the films was estimated to be 15 nm/h in our previous study.[19] Resistivity was measured by a four-probe method, and susceptibility was

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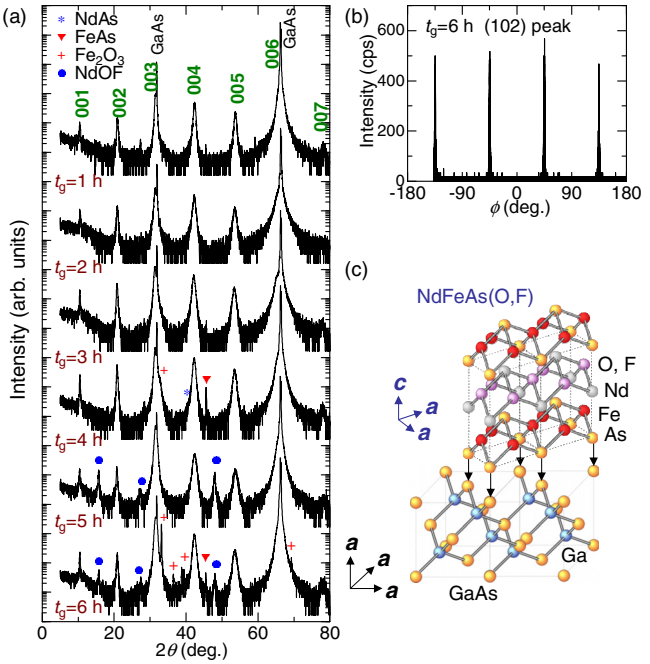

FIG. 1. (Color online) (a) Out-of-plane θ-2θ XRD profiles of films grown with different growth time t_g. All growth parameters except the growth time were identical for these films. The XRD profiles indicate that the Nd-1111 phase was grown with the c-axis perpendicular to the substrate in all films. (b) Azimuthal ϕ-scan profile of the off-axis (102) reflection of the t_g=6 h film. A clear fourfold symmetry can be confirmed. (c) A schematic drawing of the epitaxial relationship between the Nd-1111 phase and the GaAs substrate, which is consistent with the results of XRD analyses.

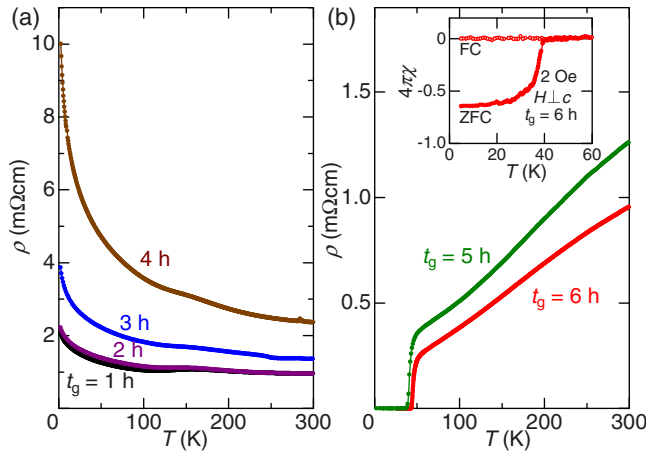

FIG. 2. (Color online) Temperature dependence of resistivity of the Nd-1111 films grown for (a) $t_g \leq 4$ h and (b) $t_g \geq 5$ h. The films grown for t_g=5 and 6 h exhibited clear superconducting transitions. T_c^{onset} and T_c^0 of the t_g=5 h film were 45 K and 38 K, respectively, while they were 48 K and 42 K for the t_g=6 h film. The inset shows the temperature dependence of susceptibility of the t_g=6 h film.

measured using a superconducting quantum interference device magnetometer (Quantum Design MPMS-7). Hall coefficient was measured under a magnetic field of 9 T.

Figure 1(a) shows out-of-plane θ-2θ x-ray diffraction (XRD) patterns of Nd-1111 thin films grown with different growth time t_g. The optimal growth condition of our previous study[19] was employed, while the substrate temperature was lowered slightly to 650 °C in an attempt to reduce the impurities that were observed in films grown with long t_g (see below). Except for the growth time, all other parameters were identical for the films shown in Fig. 1(a). As can be seen, the films grown for $t_g \leq 3$ h were single-phased and all XRD peaks except those arising from the substrate could be indexed as (00l) reflections of the Nd-1111 phase. With increasing the growth time further, however, the growth became somewhat unstable and some impurity peaks were observed in the XRD patterns. In particular, the formation of NdOF phase is obvious for the t_g=5 and 6 h films. A fourfold symmetry was confirmed for the Nd-1111 phase in all films by measuring the azimuthal ϕ-scan of the (102) peak, as shown for example for the t_g=6 h film in Fig. 1(b). These results indicate that the Nd-1111 phase was grown epitaxially on the substrate with the relation schematically shown in Fig. 1(c).

Figure 2 shows the temperature dependence of resistivity $[\rho(T)]$ of the Nd-1111 films. The film thickness that was necessary to convert resistance data to resistivity was calculated using the previously determined growth rate 15 nm/h (Ref. 19) and assuming that it does not depend on the growth time. As shown in Fig. 2(a), the resistivity of the films grown for $t_g \leq 4$ h increased at low temperature similarly to the film we reported in our previous study[19] and did not show a superconducting transition. In a stark contrast, however, the t_g=5 and 6 h films shown in Fig. 2(b) exhibited clear superconducting transitions. T_c^{onset} and T_c^0 of the t_g=6 h film were slightly higher than the t_g=5 h film, and were 48 K and 42 K, respectively. The susceptibility of the t_g=6 h film, which is shown in the inset to Fig. 2(b), confirms also a superconducting transition at about 40 K.

The difference between the $t_g \leq 4$ h and $t_g \geq 5$ h films can be attributed to F-contents. Figure 3 shows the temperature dependence of Hall coefficient of the Nd-1111 films. All films exhibited a negative Hall coefficient for the temperature range investigated. The magnitude of Hall coefficient of the $t_g \leq 4$ h films, which did not show a superconducting transition, increased steeply below about 200 K. On the other hand, the Hall coefficient of the t_g=5 and 6 h films had a much weaker temperature dependence. This change in the behavior of Hall coefficient corresponds quite well to the difference between nondoped and F-doped single crystals of Nd-1111,[20] suggesting that the films grown for t_g=5 and 6 h were doped with fluorine. Interestingly, the change in the behavior of Hall coefficient was rather abrupt between t_g=4 and 5 h. The results of EPMA is consistent with this observation because no fluorine was found in the $t_g \leq 4$ h films while the t_g=5 and 6 h films contained a certain amount of fluorine.

Next, we would like to discuss why fluorine was observed only in the films that were grown with long t_g. Figure 4 shows the Auger depth profile of the t_g=6 h film, which is a plot of the intensities of the Auger signals as a function of the sputtering time t_{sp}. The interface between the film and the

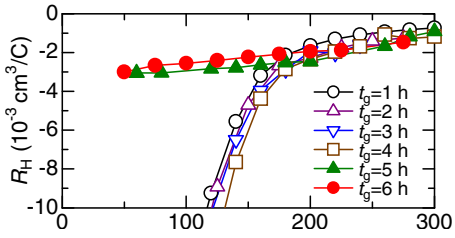

FIG. 3. (Color online) Temperature dependence of Hall coefficient of the Nd-1111 films.

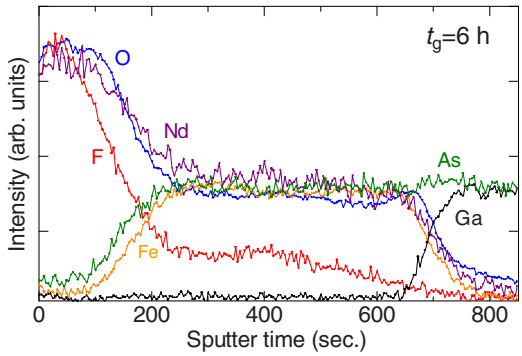

FIG. 4. (Color online) Auger depth-profile analysis of the Nd-1111 film grown for 6 h. The intensity of the Auger signal is plotted as a function of sputtering time.

substrate is evidenced by a rise in the Ga signal, and it can be seen that the contents of Nd, Fe, As, and O are nearly constant above the interface up to a certain thickness. The presence of fluorine is also confirmed, which is consistent with the conclusion of Hall coefficient and EPMA measurements. Very interestingly, however, we observed steep increases in Nd, O, and F contents near the surface ($t_{sp} \lesssim 200$ s), which was accompanied by depletion of Fe and As contents. This implies that the NdOF phase, that was observed in the XRD analyses of the $t_g = 5$ and 6 h films, was formed at the end of the film growth. Indeed, the reflection high-energy electron diffraction pattern that was monitored during the growth suggested that Nd-1111 was grown until $t_g \sim 4$ h, while a different phase, presumably NdOF, was dominant for $t_g \gtrsim 4$ h.

The change in the dominantly growing phase from Nd-1111 to NdOF at $t_g \sim 4$ h was entirely unexpected for us because none of the processing parameters were changed during the growth. However, we point out that the films were grown in an atmosphere that was probably quite excessive in fluorine. This is because NdF_3 was used as the source of Nd and F, which means that the supplied amount of F was three times larger than Nd. Therefore, what was unusual might be not the formation of NdOF but rather the Nd-1111 phase during the early stage of the film growth. It has been reported that fluorine can react with GaAs forming GaF_3 when GaAs is exposed to a F-containing vapor and the formed GaF_3 sublimates above about 550 K (about 280 °C).[21] We think that the same reaction took place at the early stage of the film growth, and the GaF_3 phase had immediately sublimated because the substrate temperature was 650 °C. This had a consequence of regulating the amount of fluorine, and the Nd-1111 phase had grown. With the increase in the film thickness, however, reaching the GaAs surface became increasingly difficult for fluorine, and some of the fluorine remained unconsumed. When the amount of fluorine exceeded than a certain level, the growth of NdOF was thermodynamically more favorable, causing the change in the dominantly growing phase.

The present model can explain why the dominantly growing phase changed with the growth time. However, one would expect then that a F-doped Nd-1111 film with no NdOF should be obtained when the growth is stopped at $t_g \sim 4$ h. Nevertheless, the results of Hall coefficient and EPMA measurements indicate that this is not the case. A possible explanation for the lack of fluorine in the $t_g \leq 4$ h films is that fluorine may diffuse easily through Nd-1111 at high temperature and had escaped from the film after the supply of NdF_3 was stopped to terminate the growth. The NdOF phase that was grown in the $t_g \geq 5$ h films may have worked as a cap layer and had prevented the loss of fluorine. In this respect, it is interesting that Kidszun *et al.*[18] had mentioned that the formation of LaOF at the surface is a typical feature in their F-doped La-1111 films.

In summary, we have grown superconducting films of Nd-1111 on GaAs substrates. The as-grown films exhibited superconducting transitions when the growth time was sufficiently long with T_c^{onset} and T_c^0 up to 48 K and 42 K, respectively. While the films grown for $t_g \leq 3$ h were single-phased, we found a NdOF layer near the surface of the films that exhibited superconducting transitions. We think that this is because our films were grown in an excess supply of fluorine but the presence of the cap layer may have played an important role to realize an as-grown superconducting film.

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