Preparation of superconducting films by metal organic deposition

— Research and development towards a fault current limiter and other electric devices —

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For the application of oxide superconductors to power-electric and microwave devices, it is necessary to form oxide superconductors into films and tapes. Since oxide superconductors are fragile and processing resistant, establishing a thin film processing technology for oxide superconductors is important. In this article, we describe our approach to developing such technology with an example that involves the processing of high quality large-size superconducting thin films by metal organic deposition (MOD) for the realization of a fault current limiter. MOD is a simple and low-cost processing technology for metal oxide thin films, which are prepared by dipping a substrate in a coating solution and firing the substrate.

Keywords : Metal organic deposition, superconductor, thin films, fault current limiter, microwave devices, coated conductor

1 Background of the research

1.1 High-temperature oxide superconductor and its application to a fault current limiter (FCL)

The high-temperature oxide superconductor that was discovered in 1986 was later found that its critical temperature (temperature at which superconductive condition is achieved and the electrical resistance is zero: T_c) can be increased to 90 K with the discovery of perovskite-type compound $YBa_2Cu_3O_7$ (hereinafter will be called YBCO), and the expectation for its practical application rose since it can be used with low-cost liquid nitrogen (boiling point 77 K) instead of expensive liquid helium (boiling point 4 K). For example, if this material is processed into power transmission cables, the loss due to resistance during power transmission can be reduced, and it was calculated that the transmission loss can be kept at about half compared to copper wire even considering the energy needed for cooling.[1]

Various applications and devices, not just power transmission cables, can be realized by processing the superconductor into thin film form. One such device is the SN transition type (thin film type) fault current limiter (FCL). As it will be explained in chapter 2, FCL is a new kind of electrical device that instantly inhibits large overcurrent that may occur due to lightning strikes or tree falls on the transmission or distribution lines, thus facilitating the shutoff of accidental current (Fig. 1).[1][2] Since the thin film type FCL (Fig. 2) is highly reliable and is capable of handling high voltage and large current, there is expectation for development toward high-volume interconnection of distributed power supply sites using low-cost superconducting film.

1.2 Metal organic deposition (MOD) method

The authors had been engaging in the development of ceramic thin film manufacturing process by the metal organic deposition (MOD) method before the discovery of high-temperature superconductors. MOD is a method of “coating and firing” where the metal organic compound containing the constituent elements are dissolved in an organic solvent, this solution is coated onto a substrate, and heat treatment is done to burn off the organic components to form the metal oxide film (Fig. 3).[3][4]

Since the MOD method is comprised of simple processes of “coating and firing” and does not require a large-scale device that produces high vacuum or high voltage, it has the following characteristics: (1) it is easy to accurately control the chemical composition of the film, (2) it uses relatively low temperature in the process, (3) it can be applied to large surface area substrates of various forms as well as tapes of long length, and (4) it has low environmental load since it emits only steam and carbon dioxide during complete combustion and does not emit harmful substances such as hydrogen fluoride as in the MOD method that uses metal trifluoroacetates as a raw material (TFA-MOD).[5]

This paper describes the approaches and methods that were employed to achieve the goal for meeting the product requirement. The technology was developed to create a high-

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quality large-surface-area superconducting film using the MOD method for application to FCL, under "R&D of the Core Technology for Superconducting AC Equipment"[1] funded for the Technological Development for Diversification of Power Source of the New Energy and Industrial Technology Development Organization (NEDO) and others.

2 Necessity for device against accidental current such as FCL, and the required specification for the superconducting film in the thin film type FCL

It was mentioned in the previous chapter that one of the applications of the superconducting thin film is to the thin film resistive-type FCL. To meet the demands of electric power deregulation and power shortage, the grid interconnection is promoted in which the distributed power supply such as excess power from home generated sources are connected and operated using the distribution lines of the electric power companies. When the distributed power supply sites are connected, in cases of short-circuit accidents as shown in Fig. 1(a), large overcurrent (accidental current or fault current) flows through the grid system instantly, and this may cause whole area blackout, damage the distributed power generators, and harm power appliances. To avoid such accidental damages, expensive additions must be made to facilities such as changing the existing distribution lines and

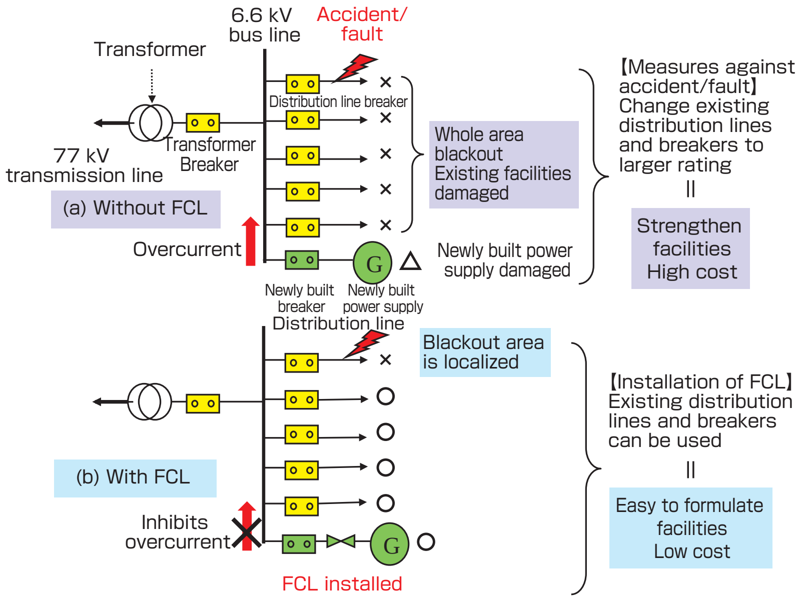

Fig. 1 Installation of FCL in distributed power supply site

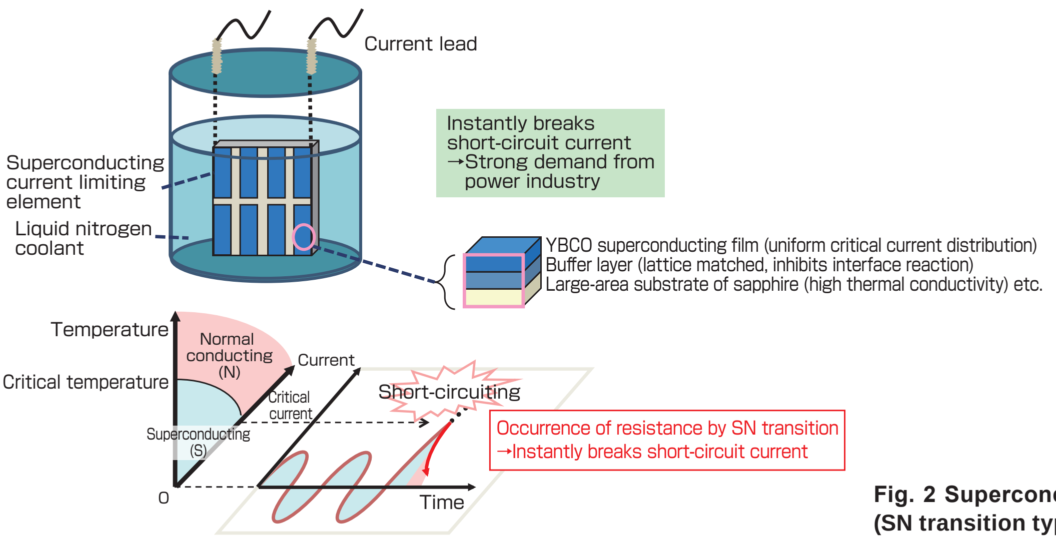

Fig. 2 Superconducting thin film FCL (SN transition type)

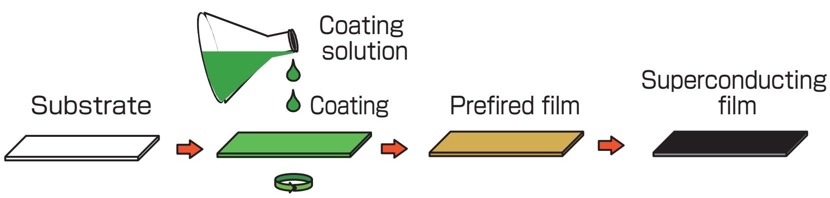

Fig. 3 Metal organic deposition (MOD) method

breakers to ones with larger ratings. In contrast, when FCLs are introduced as shown in Fig. 1(b), the existing distribution lines and breakers can be used and the facilities can be laid out readily. Therefore, the realization of such FCLs is eagerly awaited.[1] Here, FCL is a device that inhibits the overcurrent to flow into the circuit to protect the power network system (distribution and main lines) from fault current.

Currently, passive (autonomous action) FCLs including the thin film resistive-type and rectifier-type, as well as active FCLs such as the semiconductor switch type and arc driven type are being developed. The thin film resistive-type FCL (Fig. 2) is a type of passive FCL that uses the phenomenon where the superconducting thin film changes instantly from superconducting to normal conducting states and large resistance is generated when the overcurrent flows through the superconducting thin film (this phenomenon is called the SN transition or quenching) to inhibit the fault current.[6] Since there are no moving parts in this method, it is reliable compared to active FCLs. Since the series-parallel arrangement of superconducting film is capable of handling high voltage and large current, there is expectation for the application to high-volume interconnection of distributed power supply sites using the low-cost superconducting film.

The functions required for the superconducting film for thin film resistive-type FCLs are as follows.

(1) Large critical current (current can flow in the superconducting state)

→ Critical current density (J_c: hereinafter, critical current per 1 cm^2 of cross section at 77 K) must be high and the thin film be wide

(2) When it shifts to a normal conducting state, it must have high resistance and produce high voltage

→ Thin film must be long in the direction of the current

The width and length of the superconducting film are related to the current and voltage, respectively, and the loss by the number of steps to obtain series-parallel arrangement and connection resistance increases as the number of sheets of superconducting film increases. Therefore, a superconducting film with high J_c and a large surface area is necessary. The developmental goals of the “R&D of the Core Technology for Superconducting AC Equipment” funded for the Technological Development for Diversification of Power Source were as follows:[7]

- High critical current density (J_c > 1,000,000 A/cm^2)
- A large surface area (10 cm × 30 cm)

Here, the J_c value of the superconducting film is strongly dependent on the microstructure of the thin film, and it is necessary to have a single-crystal film where the YBCO particles are arranged three dimensionally to achieve high J_c. Therefore, it is necessary to manufacture a single-crystal superconducting thin film using the single-crystal with good lattice match (small difference of lattice constant) with YBCO as a substrate, and then epitaxially grow the YBCO on such a substrate. As it will be mentioned later, the sapphire (single-crystal alumina) substrate is highly regarded as the substrate for superconducting film for FCL from the perspective of thermal shock resistance and thermal conductivity. The largest size of commercially available sapphire was 10 cm × 30 cm. Since sapphire has poor lattice match with YBCO (about 10 % mismatch) and reacts with YBCO at high temperature, it is necessary to form an appropriate buffer layer between the two. Also, the superconducting film must be thick to increase the critical current, but the thermal expansion coefficient of YBCO (13 × 10^{-6}/K) is about twice that of sapphire (5~7 × 10^{-6}/K).[8][9] When the film thickness of YBCO surpasses 300 nm (critical film thickness), micro-cracks may occur due to heat stress when cooling from the deposition temperature (700~800 °C), and therefore, the film thickness that can be obtained with sapphire is 300 nm or less.

3 Comparison of the MOD method and conventional large-area deposition technology and the scenario to realize the goal

As it is clear from chapter 2, the establishment of synthesis technology for large-area superconducting films with high J_c is necessary for the development of thin film resistive-type FCLs. Meanwhile, the authors have been engaging in the research of a YBCO thin film preparation process using the MOD method immediately after the discovery of YBCO. In this chapter, we shall describe the R&D scenario to achieve the goal for the product requirement extracted in chapter 2, when preparing the large-area superconducting film by the MOD method for FCL application, after comparing the MOD and the conventional large-area deposition technologies.

3.1 Comparison of the MOD method and other large-area deposition technologies[3][4]

As shown in Fig. 3, the MOD method and the conventional large-area deposition technologies for metal oxides can be compared as follows.

1) Conventional technology

(1) Gas phase method (vacuum evaporation, pulsed laser deposition (PLD), sputtering, and chemical vapor deposition): The component atoms (molecules) are dissociated in the gaseous phase and then deposited on a substrate. Dense and good quality epitaxial film can be manufactured.

(2) Liquid phase method (slurry coating, sol-gel): The slurry, in which the powder of the target substance is dispersed in a solvent or a sol where a metal alkoxide is hydrolytically polycondensed, is coated onto a substrate, dried, and fired to manufacture a ceramic film.

2) Problems of the conventional method

(1) The gas phase method requires the simultaneous control of the processes of gas production and deposition on the substrate, and therefore, controlling the composition and achieving large surface areas are difficult. Also, since high vacuum and high voltage are necessary, expensive facilities and a large amount of power are required, thus making the process costly and energy consuming.

(2) As powder or gel formed by drying sol is fired, the liquid phase method results in a polycrystalline, non-oriented film with low performance.

It is possible to obtain an epitaxial film with high J_c by the gas phase method, but it is expensive and may generate non-uniformity in a large surface area. Conventionally, the maximum size of a YBCO film manufactured by the gas phase method is: 20 cm in diameter (with a non-deposited area in the center) and 10 cm × 20 cm (substrate transfer in one direction) by co-evaporation;[10] 7 cm × 20 cm by PLD;[12] and 7 cm in diameter by sputtering.[13] On the other hand, the liquid phase method enables the production of a low-cost, uniform, large-area film, but it will be polycrystalline, non-oriented, and have low J_c.

3.2 Scenario to achieve the goal

In this study, R&D was conducted using a scenario divided into the following two stages to achieve the goal to fulfill the product requirement extracted in chapter 2.

I. Demonstration of YBCO thin film manufacturing and achievement of high J_c

II. Deposition of a high-J_c large-area YBCO film

When discussing the research of the superconducting film deposition by the MOD method in chronological order, initially only Scenario I was the goal of development. There was fierce international competition to develop the superconducting film deposition technology by a solution method immediately after the discovery of the YBCO superconductor. The authors were able to demonstrate the zero resistance of the YBCO film ahead of other research institutions and were able to file the patent. Immediately after the discovery of the YBCO superconductor, development in Josephson elements for thin film application and superconducting wire rods, coils, magnets, and others in the thick film application were discussed, but the achievement of high J_c (>1 000,000 A/cm^2) was required in all these applications. Figure 4 shows the diagram of the research scenario at this point.

When the firing temperature is high, a chemical reaction occurs at the interface between the YBCO film and the substrate, and therefore a low-temperature process was developed to inhibit this interface reaction. Then, a lattice-matched substrate that became available due to low-processing temperature was used to increase the orientation capability of the YBCO film, epitaxial film was formed unexpectedly even though it was through a solution method, and high J_c was obtained. The outline of this process will be discussed in the next chapter.

When it became apparent that the epitaxial YBCO film could be manufactured in Scenario I, the talks began of power deregulation and large-volume interconnection of distributed power supply sites. Since the superconducting film FCL became hopeful in strengthening the durability of the electrical devices for high-volume interconnection of dispersed power at low cost, the core technology for "epitaxial YBCO deposition and achievement of high J_c" obtained in Scenario I was expanded to set Scenario II. However, many difficulties were predicted in manufacturing the large-area YBCO film with high J_c all at once, and the R&D was done concurrently to achieve the goals of II-1 and II-2 as follows. Ultimately, Goal II-3 would be achieved to fulfill the product requirement extracted in chapter 2.

II-1 Achievement of large-area YBCO deposition on lattice-matched substrates

II-2 Multilayer deposition of buffer and superconducting layers on sapphire (lattice-mismatched) substrates

II-3 Manufacture of a large-area film with superconducting/buffer/sapphire multilayers

This scenario is shown in Fig. 5 and the outline will be explained in chapter 5. Table 1 shows the outlines of the elemental technologies that were necessary to achieve the goals in Scenario I and II for manufacturing the superconducting film, and the elemental technologies that played a major role in achieving the goals are framed by thick lines.

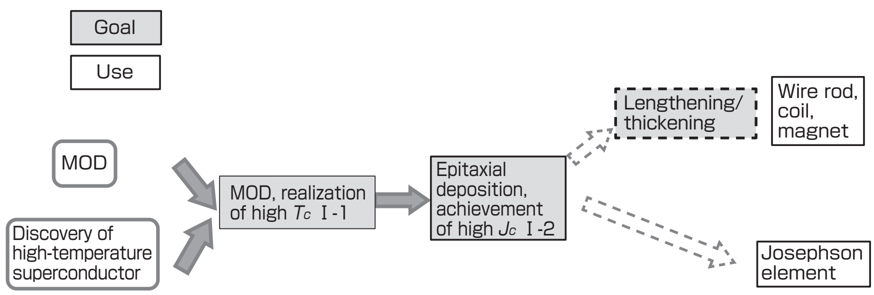

Fig. 4 Scenario I for the manufacture of high-J_c superconducting film by MOD

Table 1. Elemental technologies to achieve the goals in Scenario I and II for the manufacture of superconducting film

GOAL	SUBSTRATE, TYPE, SIZE	BUFFER LAYER	SOLUTION	COATING	PREFIRING	FINAL HEAT TREATMENT	USE
I -1 : MOD, realization of high T_c	Selection of low-reactive substrate · YSZ·12 mmΦ, 25x25 mm²	–	Search of raw material and solvent	Dip coating	Thermal decomposition	Search of heat treatment condition in oxygen	
I -2 : Achievement of high J_c	Lattice-matched single crystal STO·5x10 mm²	–	Solution tuning	Spin coating	Thermal decomposition	Development of low-oxygen low-temperature process	(Josephson element)
II-1 : Primary achievement of large surface area	Large-area lattice-matched single crystal · STO, LAO·2 cmΦ, 5 cmΦ		Solution tuning	Spin coating	Thermal decomposition	Low-oxygen low-temperature process (infrared heating)	
II -2 : Consideration of multilayer process	Lattice-mismatched single crystal· sapphire · 2x2 cm²	CeO_2 vapor deposition	Solution tuning	Spin coating	Thermal decomposition	Low-oxygen low-temperature process (tubular furnace)	
II -3 : Achievement of large-area multilayer	Large-area lattice-mismatched single crystal·sapphire · 1x12 cm², 3x21 cm², 10x30 cm²	Large-area CeO_2 vapor deposition	Solution tuning	Large-area spin coating	Thermal decomposition	Low-oxygen low-temperature process (large-area tubular furnace)	FCL
II -4 : Achievement of low Rs, patterning	Low permittivity substrate·LAO, LSAT · sapphire 2x2 cm², 5 cmΦ	[CeO_2 vapor deposition]	Solution tuning	Spin coating	Irradiation· thermal decomposition (ELAMOD)	Low-oxygen low-temperature process	Microwave filter
II -5 : Lengthening/ thickening, Achievement of high I_c	Textured metal· Ni-W etc. 1 cm width	CeO_2 vapor deposition	Coating solution for thick films, flux pinning	Dip coating etc.	Irradiation· thermal decomposition (ELAMOD)?	Low-oxygen low-temperature process	Wire rod

4 Demonstration of YBCO thin film manufacturing and achievement of high J_c

In this chapter, the outline for achieving the high J_c in Scenario I shown in Fig. 4 will be explained.

4.1 Preparation of the solution and the demonstration of YBCO deposition by heat treatment in oxygen

As shown in Table 1, to achieve Goal I-1, the search for starting materials and solvents for the coating solution, the pursuit of heat treatment conditions, and the selection of low-reactive substrates were the major developmental elements.

In general, the metal organic compounds with different electronegativity tend to have different solubility, and it is difficult to prepare a homogeneous solution in a multicomponent system. In this research, solvent search was conducted using the organic compounds with characteristic structures (ones with side chains or acting as ligands) as starting materials and changing the types of solvents (hydrocarbon, alcohol, acid, ketone, aldehyde, ester, and nitrogen compounds) or their chain lengths. As a result, we were able to create a coating solution in which the Y, Ba, and Cu were homogeneously dissolved in high concentration. This solution was applied to the substrate, thermally decomposed at 500 °C in an ambient atmosphere to form a prefired film composed of Y_2O_3-$BaCO_3$-CuO. The final heat treatment and solid-phase reaction were done at 950 °C in oxygen as in the sintered compact, and we succeeded in demonstrating the YBCO film preparation[14][15] and obtained the basic patent for the solution and the manufacturing method. However, since the final heat treatment temperature was high, we were unable to obtain a YBCO film on the lattice-matched single-crystal substrates with a perovskite structure such as strontium titanate ($SrTiO_3$, lattice mismatch: about 1 %) since

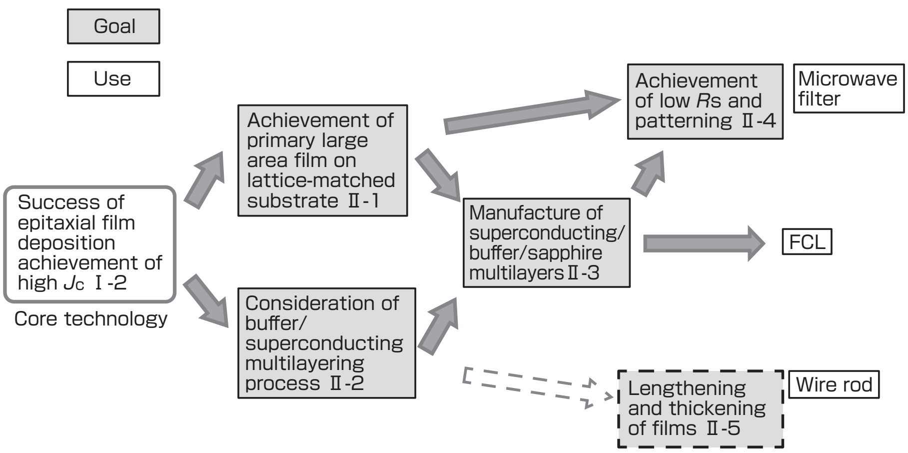

Fig. 5 Scenario II for the manufacture of large-area superconducting film for FCL

it reacted with $BaCO_3$ in the prefired film. We obtained T_c = 90 K only when the yttria-stabilized zirconia sintered compact with low reactivity was used as the substrate, but the film was polycrystalline, and the J_c at liquid nitrogen temperature (77 K) was low (~1000 A/cm^2).[16]

4.2 Development of a low-temperature process and achievement of high J_c

The development of a low-temperature process using low-oxygen pressure was the most important point in achieving Goal I-2.

Since the superconductivity is lost when the high-temperature oxide superconductor is deprived of oxygen, it was conventionally fired in oxygen. The authors obtained the hint from the study by Kishio *et al.*,[17] and considered that the valence control of functional oxides that contain transition metals such as YBCO was important, and heat treatment must be done by controlling the oxygen partial pressure (pO_2) and temperature (T). Therefore thermal analysis was conducted by changing the pO_2 for the powder obtained by thermal decomposition (or prefiring) of the coating solution. As a result of x-ray diffraction of the product, it became apparent that the production temperature of YBCO could be decreased by 100 °C or more by using low oxygen pressure.[18]

In the heat treatment at maximum temperature of around 700 °C, the reaction between the YBCO and a lattice-matched single-crystal substrate such as $SrTiO_3$ could be sufficiently suppressed, and the YBCO film was formed on the $SrTiO_3$ substrate. To improve the uniformity and reproducibility of the thickness of the film product, the solution was applied using a spin coater[19] and prefiring was done at 500 °C in an ambient atmosphere.

Next we succeeded in decreasing the temperature by about 200 °C from the maximum temperature of the conventional heat process by optimizing the oxygen partial pressure and the heating rate for the final heat treatment of the prefired film (development of the low-temperature process). Figure 6 shows the schematic representation of the stable range of YBCO and copper oxides (Cu_2O-CuO) on the Ellingham diagram, with the logarithm of oxygen partial pressure (pO_2) and the reciprocal of temperature ($1/T$) as the two axes (orientation will be discussed in the next chapter).[20] Here, the conventional heat process in oxygen corresponded to Route I-1, while the low-temperature process to Route I-2. Since low-oxygen pressure was used in Route I-2, the non-superconductor $YBa_2Cu_3O_6$ with less oxygen was produced in the final heat treatment, but by switching to 1 atm oxygen after the final heat treatment and allowing the oxygen to be incorporated into the crystal during cooling, it converted to superconductor $YBa_2Cu_3O_7$. Moreover, as an amazing finding at the time, the YBCO film manufactured in Route I-2 grew epitaxially on the substrate even though it started from the solution, and a J_c of 1,000,000 A (=1MA) /cm^2, which is equivalent to that of the YBCO film made by the gas-phase method was achieved at 77 K. Hence, Goal I-2 was achieved.[21][22]

5 Deposition of a large-area YBCO film with high J_c

In this chapter, setting the “success of epitaxial film formation, achievement of high J_c” of Scenario I-2 as core technology, the outline up to the realization of high- J_c large-area film by Scenario II as shown in Fig. 5 is explained.

The YBCO film prepared on $SrTiO_3$ substrate in chapter 4 was of a small size of 5 mm × 10 mm. Due to the reactivity of the substrate and the film as well as due to lattice mismatch, it was difficult to concurrently achieve the deposition on a large-area sapphire (single-crystal alumina) substrate that was desirable for FCL, as there was strong demand and desire to test the performance of the large-area YBCO film as soon as possible. Therefore, it was decided that, as shown in Scenario II in Fig. 5, while attempting to primarily increase the surface area of the YBCO film on the lattice-matched substrate, II-1, the manufacture of a buffer layer on the sapphire and tuning of YBCO deposition was conducted concurrently, II-2, and the enlargement of superconductor/ buffer /sapphire layer was done afterwards, II-3.

5.1 Achievement of large-area deposition on the lattice-matched substrate

For the achievement of Goal II-1, the selection of optimal heating rate in the low-temperature process was the main issue.

When the surface area of the lattice-matched substrate was increased, J_c tended to decrease compared to the smaller

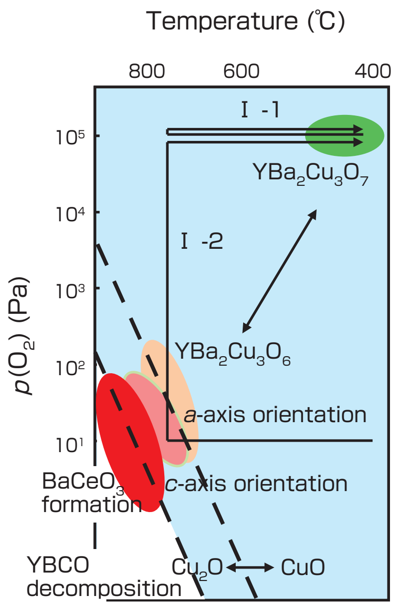

Fig. 6 Orientation and reaction of the YBCO film in the Ellingham diagram

substrate even under the same heat treatment conditions. Initially, we did not know the reason for this, but referring to the Ellingham diagram in Fig. 6, it was revealed that there were areas in which the YBCO films readily become *c*-axis oriented (orientation that the superconducting current easily flows) with high J_c around the temperature of thermal decomposition of YBCO and CuO, and areas in which the YBCO films readily become *a*-axis oriented (orientation that the superconducting current does not easily flow) with low J_c in the low-temperature side or areas of high oxygen-partial pressure, just as in the gas phase method.[23][24] Using this property, the *c*-axis oriented film is deposited in the *c*-axis oriented area by the gas phase method.[25] On the other hand, in the MOD method, since the prefired film that was once deposited underwent final heat treatment, the crystal growth of the *a*-axis grains is likely to occur locally as the substrate surface area increased as it passed through the *a*-axis oriented area in the heat process in the ordinary electrical furnace with a small heating rate. It was thought that the inclusion of the *a*-axis orientation occurred due to this phenomenon.

Therefore we introduced an infrared image furnace that enabled rapid heating. As a result of investigation on the heating rate and uniform heating conditions, the *c*-axis oriented film was obtained by rapid heating, i.e., by quickly passing the low-temperature zone where the *a*-axis orientation tended to occur and the *a*-axis oriented growth was inhibited. The YBCO film with a thickness of 700 nm manufactured on the lattice-matched $LaAlO_3$ (LAO, mismatch about 2 %) with a diameter of 5 cm was extremely dense and smooth, and J_c measured by the inductive method was extremely high (>2 MA/cm^2).[26][27] Even with rapid heating, since YBCO and LAO are lattice matched and the thermal expansion coefficients are close (YBCO: 13 × 10^{-6}/K; LAO: 12.6 × 10^{-6}/K[9]), no cracks occurred. Thus,it was possible to obtain a YBCO thick film with high J_c on a lattice-matched LAO substrate. However, the maximum size that can be manufactured for a LAO substrate is about 5 cm in diameter, and a larger surface area cannot be obtained. Also, the thermal shock resistance and heat conductivity are low, and the substrate tends to be damaged due to heat stress when it is cooled in liquid nitrogen in the quenching process, and therefore it is considered unsuitable for FCL application.

5.2 Formation of a buffer film on a sapphire (lattice-mismatched) substrate

As a substrate material for superconducting films for FCL application, sapphire (single-crystal alumina) is optimal since heat conductivity and thermal shock resistance are high and large-surface area substrate is available. However, sapphire chemically reacts with YBCO, has a different crystal structure, and has large lattice mismatch (about 10 %), and these make the direct epitaxial growth of YBCO difficult. Therefore, similar to the gas phase methods,[10]-[13] CeO_2 (lattice mismatch of about 1 %) was used as the buffer layer to mitigate the lattice mismatch as well as to inhibit chemical reaction.

When the CeO_2 buffer layer was formed by a vacuum vapor deposition method by changing the deposition conditions (temperature, deposition rate, oxygen pressure, and plasma gasification conditions) on the sapphire substrate, the orientation of the CeO_2 could be arranged in desirable directions (100) by plasma gasification of oxygen by a radiofrequency (RF) antenna and by increasing the substrate temperature. Then, the CeO_2 buffer layer with a smooth surface at nanometer level could be obtained.[28][29]

Concurrent to the buffer layer deposition, we attempted tuning with the YBCO deposition by the MOD method on the buffer layer. Although the heat treatment condition was about the same as on the lattice-matched substrate, when CeO_2 was used for the buffer layer, the production of $BaCeO_3$ by reaction with YBCO became an issue. When $BaCeO_3$ is produced, the amount of Ba in the film decreases, and not only does the metal composition ratio depart from 1:2:3 but also the crystallization property of YBCO decreases and the superconductivity degrades significantly. When we investigated the heat-treatment condition of the YBCO film when the CeO_2 buffer layer was used, it was found that $BaCeO_3$ was likely to be produced in high temperature or low oxygen partial pressure side, as shown in Fig. 6. It was also found during the optimization of the YBCO deposition condition on the CeO_2 buffer layer, that although CeO_2 had small lattice mismatch with YBCO, it had a fluorite-type crystal structure that was different from YBCO, and the YBCO crystal growth rate became relatively small on CeO_2. Therefore, no rapid heating using the infrared image furnace was required as in the lattice-matched substrate, and only heating with a tubular furnace was necessary. As a result of tuning the buffer layer deposition method and the heat treatment conditions, we succeeded in depositing YBCO with high J_c at maximum heat-treatment temperature of about 750 °C, with a CeO_2 buffer layer of 40 nm (achievement of Goal II-2).[30][31]

5.3 Achievement of large-area superconducting/buffer/sapphire multilayers

Next, we attempted to deposit the buffer layer on a large-area sapphire substrate and to form the superconducting multilayer on this layer. Here, the key issue was the uniformity of thickness of both layers deposited and of temperature and atmosphere of heat treatment.

For the buffer layer deposition, two vapor deposition sources were installed to improve uniformity, the decrease of substrate temperature was prevented by devising a heater and shield, and oxygen was plasma activated by a RF antenna. By increasing the power of RF and maintaining the substrate temperature high, we obtained a CeO_2 film with a large surface that was smooth and uniform at nanometer level.[28][29]

We introduced a spin coater to handle large substrates for the large-area YBCO deposition, and a coating solution that was tuned for viscosity and evaporation rate to ensure even film thickness was applied. Next, in the prefiring process, totally uniform prefired film was obtained using a large muffle or tubular furnace in which the heating rate and the atmosphere were controlled. From the result of subchapter 5.2, it became apparent that rapid heating using the infrared image furnace was not necessary for the final heat treatment, and we succeeded in manufacturing a high-performance YBCO film on a large-area sapphire substrate of 10 cm × 30 cm size, by conducting precise temperature and atmosphere control using a large tubular furnace with high temperature uniformity (Fig. 7). It was on average J_c = 2.6 MA/cm^2 as obtained in the inductive method, and the uniformity of average J_c within ±20 % range was obtained for the majority of the measurement points. The goal value of the project in chapter 2 was achieved (II-3).[31]-[33]

6 Later development

Up to the previous chapter, we described the development of the synthesis technology of the large-area superconducting film by the MOD method. In this chapter, we shall discuss the later development: (1) the result of manufacturing the fault current limiting element using the superconducting film developed in this research, in a joint research with external institutions (companies, universities, and the Central Research Institute of Electric Power Industry) and a research group within AIST (jointly with Energy Technology Research Institute), and then creating a prototype FCL by a series-parallel arrangement and conducting the current limiting test; and (2) the application to microwave devices and wire rods. Please refer to the references for details.

6.1 Prototype FCL test

The superconducting films for the element were prepared by depositing on the CeO_2/sapphire substrate of 3 cm × 21 cm size with high throughput and uniformity, and a gold-silver alloy shunt layer with high resistance was formed to increase the voltage produced after quenching.[34]

(1) Joint research: mockup device (Fig. 8)
The 6.6 kV class single-phase FCL unit, in which six units of two parallel elements were connected in series, was used to limit the peak current of 11.3 kA to 4.5 kA. Based on this result, conceptual design of the 6.6 kV class triple-phase FCL was done.[35]

(2) AIST research:
The 500 V/200 A single-phase FCL unit that used the non-inductive shunt resistance developed by AIST was used to limit the peak current of 3.5 kA to 770 A.[36]

The cost of the large-area superconducting film used for FCL in the dispersed distributed power supply site was calculated, and it was shown that in the future it will be lower than the target cost of realization.[37]

Based on these results, the technological transfer to companies of the large-area superconducting film manufacturing process is being promoted.

6.2 Application to microwave devices and wire rods and tapes

(1) Microwave filter for mobile communication base station
Since the high-temperature superconductor has lower surface resistance than metal in the microwave range, call-enabled areas can be expanded and effect of electromagnetic wave can be decreased by increasing the communication quality by incorporating a filter made from a superconducting film into the mobile communication base station system.[38][39] Here, the goals (II-4) required for the superconducting film are double-sided deposition on a large-area (5 cm in diameter), low-permittivity substrate, low surface resistance, and patterning. The authors obtained the following results for the application to this field.

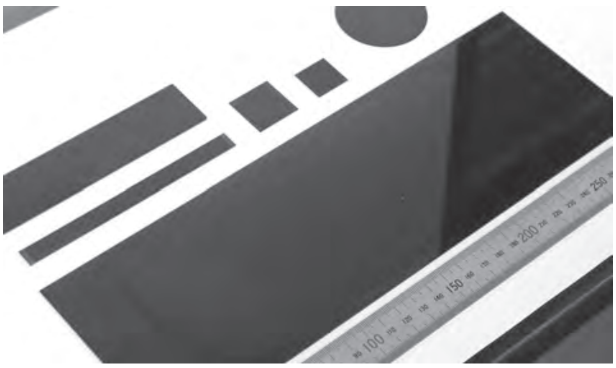

Fig. 7 Large-area YBCO films manufactured on substrates of various forms

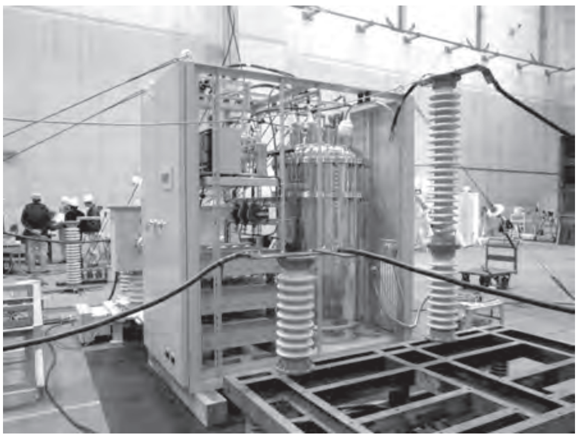

Fig. 8 6.6 kV single-phase FCL prototype

a. Manufacture of microwave filter on a 2 cm × 2 cm $LaAlO_3$ substrate and verification of filter performance[40]
b. Achievements of YBCO deposition on a 5 cm diameter $LaAlO_3$ substrate and low surface resistance[41]
c. Achievements of double-sided YBCO deposition on a 5 cm diameter CeO_2/sapphire substrate and low surface resistance[42]
d. Possibilities of YBCO deposition by excimer-laser-assisted MOD (ELAMOD) and concurrent patterning[43]

(2) Application to wire rods and tapes
The YBCO superconducting wires and tapes with long length and thickness were achieved by chemical vapor deposition (CVD) and TFA-MOD using trifluoroacetate (TFA) as the raw material . The MOD method discussed in this research is called the fluorine free (FF) MOD method since it does not include harmful fluorine in the raw material, and is expected to become a manufacturing method for superconducting wire rods and tapes at low cost and low environmental load. The authors have been conducting research with the goal of developing high critical current (I_c) films (high J_c and thick film) on oriented metal substrates that can be made long (Goal II-5), and the following results have been obtained to present.

a. Development of a thick coating solution: 0.8 μm was achieved by a single coat and firing[44]
b. Manufacture of a thick film by repetition of the whole MOD process that includes coating, prefiring, and final heat treatment: manufactured a 4-μm-thick epitaxial film
c. Achievement of high I_c (>200 A/cm) by introducing pinning: highest for a FF-MOD film[45]

7 Summary

This paper introduced the following two scenarios and elemental technologies that were employed to achieve the goals to meet the product requirements for the technology for a high-quality, large-area superconducting film by the MOD method for the purpose of FCL application.

I. Verification of YBCO thin film manufacturing and achievement of high J_c
II. Deposition of a high-J_c, large-area YBCO film

In Scenario I, the main topic was the preparation of a homogeneous coating solution based on solution chemistry and the development of a low-temperature process using low oxygen pressure that is based on solid physical chemistry. Even though we started from the solution, we obtained a high-J_c film that grew epitaxially on the substrate.

On the other hand, in Scenario II, the approach taken was first contemplating the enlargement of the YBCO film on the lattice-matched substrate, II-1, and, concurrently, conducting the manufacture of the buffer layer on lattice-mismatched sapphire and the tuning of YBCO deposition, II-2. Afterwards, a large surface area was achieved for the superconducting/buffer/sapphire multilayers, II-3. In executing this approach according to the development plan, there were researchers who were specialists of gas phase deposition and those who specialized in liquid phase deposition within the group, and the two sets of researchers collaborated and offered good feedback. It was also crucial that we were able to procure manufacturing and evaluation devices that could handle large substrates at the appropriate time.

These approaches are utilized in the applications to microwave devices and wire rods and tapes.

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Discussions with Reviewers

1 Overall

Comment (Hiroshi Akoh, Thermal Management Materials and Technology Research Association)

This paper focuses on the target of electrical application of a high-temperature oxide superconductor to the fault current limiter, and builds the scenario for its development and shows the selection and combination of the elemental technologies. I think it is valuable as a *Synthesiology* paper.

Comment (Tetsuhiko Kobayashi, AIST)

This paper is about the creation of a large-area superconducting film for application to FCL, and I recommend its publication in the journal.

2 Explanation of FCL

Question and Comment (Hiroshi Akoh)

In this paper, the development of FCL is given as the electric power application of high-temperature oxide superconductors. Therefore, I think it is important to show a diagram that allows the readers outside the field to grasp the image of FCL. In the paper, the structure and operational principle of FCL are shown in diagrams, and it is described in the text in chapter 2, however I think readers can more easily understand if you present a figure that shows the role and importance of FCL in the power grid system. Also, I think you can clarify the correspondence to the photograph of the device which includes the prototype FCL shown in Fig. 8.

Moreover, there is a description of “development of many types of FCLs” in chapter 1, however I think you should clarify by giving specific examples of other types of FCLs.

Answer (Toshiya Kumagai)

I added a figure that shows the role of FCL in the power grid system as Fig. 1, and inserted in the upper part of Fig. 2 a figure that shows the “FCL cooled in the cryostat” that shows correspondence to the photo of the device in Fig. 8.

I added a few examples of active and passive FCLs in chapter 2.

3 Relationship of Scenarios I and II

Question and Comment (Hiroshi Akoh)

I understand that Scenarios I and II are continuously related toward the development of FCL, however the relationship of Scenarios I and II seems to become unclear since you explain them separately in Figs. 4 and 5. I think the main point of this paper is that you succeeded in achieving high T_c and high J_c by the MOD method, and using that as core technology and advancing the R&D to achieve a large-area film and multilayer, there was considerable progress in the FCL development. I think the scenario continues to mention that the application can extend to microwave devices by achieving low surface resistance and patterning, and in the future it can be applied to superconducting wires by achieving the long length and thick thickness. What do you think of the scenario where you discuss mainly the development of FCL and then spreading out to microwave devices and superconducting wire applications?

Answer (Toshiya Kumagai and Takaaki Manabe)

The scenario of the whole paper and its main point are as you indicated. However, describing the research in chronological order, it was still unclear that FCL was the outlet when we were setting Scenario I (at the time of discovery of the high-temperature superconductor). The application to various electric power devices was a “dream,” and in reality, we conducted R&D for “high J_c” as the essential goal to realize that dream. Later, when we achieved high J_c, we could regard various devices including FCL as specific targets, and only then did we set the goal to fulfill the product requirements, build the scenario to achieve them, and then engaged in the R&D. In this paper, we focus on the application to FCL, but we have concurrently worked on the application to microwave devices to some extent. Considering these points, we shall describe Scenarios I and II separately in the figures. In Fig. 5, we specify that the “success of epitaxial deposition and achievement of high J_c” in I-2 are the core technologies in Scenario II.

4 Characteristic of the MOD method

Question and Comment (Tetsuhiko Kobayashi)

You describe in subchapter 1.2 as one of the characteristics of MOD that “(4) it has low environmental load since it emits only steam and carbon dioxide during firing,” but aren’t VOC and incomplete combustion gas produced depending on the condition?

Answer (Takaaki Manabe)

As you indicated gases such as VOC may be produced in incomplete combustion. Also, this item is not a characteristic of the MOD method compared with the gas phase method, but is the characteristic of the FF-MOD method using fluorine-free materials that was employed in this paper, in contrast to the TFA-MOD method that uses trifluoroacetate as the raw material. I added and revised item 4 to make this clear to the readers.

5 Infrared rapid heating process

Question and Comment (Hiroshi Akoh)

This is a technical question. As you describe in chapter 5, you developed the rapid heating process by infrared heating to inhibit the *a*-axis oriented growth and to obtain the *c*-axis oriented film. Were there any cracks in the film due to the difference in thermal expansion coefficients of the substrate and the film? Please explain if there were no cracks.

Answer (Takaaki Manabe)

No cracks occurred by rapid heating for the YBCO film with thickness of 700 nm on LAO. I explained that it is because they are lattice matched and their thermal expansion coefficients are close.

Also, the film on sapphire that has large thermal expansion difference tends to get micro-cracks during cooling after deposition, and the thickness of the YBCO film is limited to 300 nm or less. I added this in chapter 2.

6 Achievement of a large-area thin films and a low-temperature process

Question and Comment (Tetsuhiko Kobayashi)

To achieve a large-area thin films, you say, “a low-temperature process was developed to increase the J_c by decreasing the interface reaction between the film and the substrate and by improving the orientation.” For readers outside the field, the meaning of “decreasing the interface reaction between the film and the substrate” is difficult to understand, and I think you need some supplementary explanation.

Answer (Takaaki Manabe)

Including the point that you indicated, the description of the draft was not well organized, so I changed the description to the following: the chemical reaction occurs at the interface between the YBCO film and the substrate when the firing temperature is high → a low-temperature process was developed to inhibit the interface reaction → this low temperature allowed use of lattice-matched substrates → orientation of the YBCO film was improved using the lattice-matched substrate.