**RE123 Coated Conductors**

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RE123 superconductor is known to exhibit superconductivity at the temperature of liquid nitrogen (77 K) and also to have excellent current property in magnetic fields. Therefore, it is expected to be used for various electric applications, so R&D of the wire using RE123 superconductor is now actively promoted all over the world. We have been adopting and developing the wire of thin film type with crystal grain highly aligned in-plane, the so called RE123 coated conductor. We introduced the large apparatus and made all improvements on each process, resulting in successful fabrication of the long wire of 500 m-length with critical current of over 300 A at the rate of over 5 m / h in February 2008. It showed world record performance and reached practical level.

1. Introduction

Superconductivity is the phenomenon whereby electric resistivity of some materials suddenly vanishes when they are cooled down under certain temperature (critical temperature : Tc), different in each material. RE123 superconductor has the chemical composition of REBa2Cu3Oy (RE : rare earth elements) and so it is called ‘RE123’. It was discovered in 1987 and firstly exhibited superconductivity at the temperature of liquid nitrogen, causing the so-called ‘fever of high-temperature superconductivity’. The critical current (Ic) of RE123 superconductor, the current transported possibly in superconducting state, is extraordinarily high even in magnetic fields. Therefore, it is expected to be applied not only for the cables but also the transformers, fault current limiters, motors, and other various electrical applications and R&D of the wire using RE123 superconductor is now actively promoted all over the world.

The crystal structure of RE123 superconductor is shown in Fig. 1. Almost all superconducting current exists in Cu-O2 plane (ab-plane), hence ab-plane of crystal grains must be oriented to the current-conducting direction of wire. Furthermore, it is reported that Ic performance degrades if each axis of crystal grains have misalignment even in ab-plane. That is to say, it requires extraordinarily high technique that submicron crystal grains should be bi-axially aligned like single crystal along the long wire in several hundred meter length.

In 1991, we developed the technique of growing bi-axially textured ceramic film on the non-textured metal tape substrate with Ar+ ion beam irradiated from a particular angle. This technique is called IBAD technique, short for Ion Beam Assisted Deposition. We have succeeded in fabricating the superconducting wire, the so-called RE123 coated conductor, with high performance by epitaxially growing RE123 superconducting layer by Pulsed Laser Deposition (PLD) technique on IBAD buffer layer. In the fiscal year 2003 ~ 2007, we performed R&D for the fabrication of the RE123 coated conductors with high performance and long length at lower cost with support from the New

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Energy and Industrial Technology Development Organization (NEDO). The goal value of this project is shown in Table 1. In February 2008, we succeeded in fabricating the 500 m-length wire with $I_c$ of over 300 A. $I_c \cdot L$, it is the benchmark for performance of the superconducting wire, it was 349.6 A / cm $\times$ 503.5 m = 176,023 Am / cm. It was the world record and reached practical level of applications.

2. Development of RE123 coated conductors

2.1 Structure of RE123 coated conductors

The structure of RE123 coated conductors we have developed is shown in Fig. 2. Firstly, bi-axially textured Gd$_2$Zr$_2$O$_7$ (GZO) buffer layer is grown in the thickness of about 1.0 μm by IBAD technique on non-textured metal tape with high mechanical strength (Hastelloy : width ~ 10 mm, thickness ~ 0.1 mm). Next, second buffer layer (thickness of 0.5 – 1.0 μm) and then RE123 superconducting layer (thickness of 1.0 – 3.0 μm) is grown on IBAD layer by PLD technique. Ag is sputtered for the protection of superconducting layer and then it is annealed in O$_2$-flow atmosphere. Finally, Cu tape or Ni-Cr tape is laminated in accordance with intended use, and then polyimide tape is wrapped for insulation.

2.2 IBAD process

2.2.1 Introduction of IBAD technique

In the case of superconducting wire using RE123 superconductor, it is reported that $I_c$ performance degrade if each axis of crystal grains have misalignment in ab-plane as shown in Fig. 3). Hence, RE123 crystal must be grown epitaxially on the bi-axially textured substrate. There are mainly two techniques to fabricate bi-axially textured substrate. One is the method that Ni or Ni-W alloy tape itself is bi-axially textured by heating operation after rolling. It is called RABiTS technique, short for Rolling Assisted Bi-axially Textured Substrate. The other is the IBAD technique, which we firstly applied for fabrication of superconducting wire in 1991). IBAD is the technique that some order is added to crystals when a film is grown with ion beam of rare gas, for example Ar$^+$ ion, irradiated from a particular angle. Schematic illustration of IBAD technique is shown in Fig. 4. When some particular oxide is deposited by ion beam sputtering, if crystal growth is controlled by IBAD technique, bi-axially textured buffer layer can be grown on non-textured Hastelloy tape.
2.2.2 Fabrication of bi-axially textured buffer layer by IBAD technique

As the material for buffer layer, yttria-stabilized zirconia (YSZ) exhibited good in-plane texture by IBAD technique at first. The pole figure measurement of X-ray diffraction is used for the evaluation of in-plane texture, and $\Delta \phi$ of YSZ that is the full width of half maximum reached $15^\circ$, which is required for high $I_c$ performance. After that, Gd$_2$Zr$_2$O$_7$ (GZO) which have same crystal structure of YSZ was found to be textured sharply to $\Delta \phi = 15^\circ$ at the half thickness of YSZ layer (~1.0 $\mu$m), which lead to a large increase in speed of fabricating buffer layer.\(^3\)

For the further scale-up, we introduced the large IBAD system with world’s largest ion source shown in Fig. 5. The larger deposition area with the 1.1 m-length ion source was expected to speed-up. On the contrary, it was difficult to meet the conditions because it was necessary to balance between the intensity of assist-beam and deposition particle on the large deposition scale. We have rigorously adjusted the gas-flow or some other conditions, resulting in successful irradiation of homogeneous ion beam to the longitudinal direction of deposition area shown in Fig. 6.

We started from the preparation of 10 m-length IBAD-GZO layer, and finally fabricated the one with 500 m-length, which was the goal of NEDO project. Figure 7 shows in-plane texture respectively of the 10 m-length one and the 500 m-length one fabricated at the rate of 5 m / h. The 10 m-length one reached the $\Delta \phi = 15^\circ$ in whole length, on the contrary, the 500 m-length one degraded to the $\Delta \phi = 18^\circ$ because it took long time \(^4\). We had to slow down the rate to 3 m / h in order to get the 500 m-length IBAD-GZO layer with $\Delta \phi = 15^\circ$.

We therefore tried to polish the Hastelloy tape for the further speed-up and higher quality. For the substrate of IBAD-GZO layer, we previously used the Hastelloy tape after rolling without polishing. However, it was found by the short sample experiment that the
IBAD buffer layer using polished Hastelloy exhibited better in-plane texture than the one using non-polished one. The surface roughness of the substrate is improved by polishing process, and the crystal grains can probably align more easily on the more homogeneous surface. So we fabricated the 500-m IBAD-GZO layer after polishing by reel-to-reel large polishing apparatus. Figure 8 shows respectively the in-plane texture of 500 m-length IBAD-GZO layer on conventional non-polished substrate and polished one. It was necessary to slow down to get the 500 m-length IBAD-GZO layer with $\Delta \phi = 15^\circ$ previously, however polished substrate enabled us to speed-up to 5 m / h, which was the successful achievement of the goal of the NEDO project on IBAD process.

2.3 PLD process

2.3.1 Introduction of PLD process

There are various approaches for lamination of RE123 superconducting layer, such as PLD short for Pulsed Laser Deposition, MOD short for the Metal-Organic Deposition, MOCVD short for the Metal-Organic Chemical Vapor Deposition, and so on. We have been adopting PLD among these techniques. PLD is the technique that a thin film is grown on substrate by deposition of the particle assemblage (it is called ‘plume’), which is generated from the sintered target with it irradiated by ultraviolet pulsed laser (mainly excimer laser). There are many features of this technique. For example, the rate of deposition is dramatically high among the gas-phase approaches and the composition control for material is easy because the film is directly affected by the composition of the target. In addition, the cost of raw material is lower than other deposition processes especially in fabrication of RE123 coated conductor because the target is just the sintered bulk of material. We have deposited not only the RE123 superconducting layer but also the second buffer layer on IBAD-GZO by PLD technique.

2.3.2 Fabrication of second buffer layer by PLD technique

It was found that the lamination of CeO$_2$ layer on the IBAD-GZO layer resulted in dramatic improvement of in-plane texture by self-alignment of CeO$_2$ crystal grains. We experimented for scale-up of the fabrication of CeO$_2$ buffer layer, it is also called cap layer, by PLD technique. Figure 9 shows the dependence of laser power for in-plane texture of CeO$_2$ cap layers.
600 mJ led to the well in-plane texture and high deposition rate of the CeO$_2$ cap layer. Secondly, the multiple plumes to the longitudinal direction by laser beam scanning resulted in successful fabrication of CeO$_2$ cap layer without degrading in-plane texture. Furthermore, we tried and succeeded in the improvement of the material yield and speed-up by passing through the deposition area many times in multi-lanes. Finally, we succeeded in fabricating the 500 m-length CeO$_2$ cap layer with the in-plane texture of $\Delta \phi = 4^\circ$ in the thickness of 1.0 $\mu$m at the rate of 10 m / h on the IBAD-GZO substrate with $\Delta \phi = 15^\circ$. 5).

2.3.3. Fabrication of RE123 superconducting layer by PLD technique

RE123 superconductor exhibits different superconducting performance by its RE elements. At first, we used YBa$_2$Cu$_3$O$_y$(YBCO), which was firstly discovered among the series of RE123 superconductors. However, it was reported that GdBa$_2$Cu$_3$O$_y$(GdBCO) have the excellent critical current performance in both non-magnetic field and strong magnetic fields, so we explored the optimal condition of its deposition.

The performance of superconducting layer grown by PLD technique depends largely on the temperature and oxygen partial pressure on the deposition process. We experimented in the high oxygen partial pressure of 90 Pa compared with conventional 70 Pa, and as a result, excellent $I_c$ value was obtained around wide deposition temperature as shown in Fig. 11. In addition to high $I_c$ performance, homogeneous $I_c$ value to the longitudinal direction of wire is also important, so we checked the $I_c$ distribution by fabricating 2 ~ 5 m-length samples. As a result, it was found that the fluctuation of deposition temperature according to the drive of the target was critical for the $I_c$ property. The optimization of the driven width of the target led to the decrease of the fluctuation of deposition temperature and resulted in smaller $I_c$ distribution$^9$ as shown in Fig. 12.

Furthermore, we tried the improvement of $I_c$ performance in magnetic fields. The flux pinning by introducing the submicron non-superconducting phase into the superconducting phase is generally effective because the movement of magnetic flux is intrinsically critical for superconductors. We therefore tried to introduce the pinning center into the superconducting layer artificially by using the GdBCO target with ZrO$_2$. In addition, we experimented the mixing lamination of the GdBCO layer with the artificial pinning center which we call ‘P’ and the pure GdBCO layer which we call ‘N’. Figure 13 shows the $I_c$ value per unit thickness, which is the critical current density $J_c$, of these samples in both non-magnetic field and magnetic fields of 3 T. The improvement of $I_c$ in 3 T for the sample ‘PPP’ indicates the actual introduction of pinning
center into superconducting layer. In addition, the sample ‘NPN’ exhibits the dramatic improvement of $I_c$ in 3 T in spite of only 1 ‘P’ layer, suggesting the effective improvement of $I_c$ in magnetic fields without suppressing degradation of $I_c$ in non-magnetic field by adding superconducting layer with impurities. The TEM dark field image and electron diffraction pattern of this ‘NPN’ sample is shown in Fig. 14. These images suggest that columnar crystals of BaZrO$_3$ were precipitated in ‘P’ layer and they played the role of pinning center.

On the basis of these knowledge, we tried the fabrication of 500 m-length GdBCO layer in Feb. 2008. The substrate with $\Delta \phi = 4^\circ$ for PLD-CeO$_2$ was used. We used 3 lanes for speed-up and laminated 6 times at the rate of 40 m / h, so throughput was 6.7 m / h, to increase the thickness and $I_c$. Furthermore, the introduction of artificial pinning center into the middle 2 layers was attempted from the knowledge mentioned above. The fabrication finished in a week without trouble. After sputtering of Ag and annealing, $I_c$ of this 500 m-length wire was measured in every 70 cm with $I_c$ criterion of 1 $\mu$V / cm by reel-to-reel continuous $I_c$ measurement system. The result is shown in Fig. 15. It exhibited extraordinarily high critical current performance, that is to say not only all points except only 1 was over 300 A but also average $I_c$ was 440 A and maximum $I_c$ was 495 A$^\circ$. We, then, turned it into practical usage structure by laminating Cu tape for stability and insulating after cutting down to 5 mm-width. After that, it was winded non-inductively and end-to-end $I_c$ was measured. The end-to-end $I_c$ was 174.8 A in 5 mm-width as shown in Fig. 16, that is to say $I_c = 349.6$ A / cm, resulting in achievement of the goal of NEDO project. $I_c \cdot L$ value, that is the multiplication of $I_c$ by length and is the benchmark of the performance for the superconducting wire, reached $I_c \cdot L = 349.6$ A / cm $\times 503.5$ m = 176,023 Am / cm, which is the world’s best performance.

Table 2 shows the progress in laminating GdBCO layers by PLD technique from 2007 to 2008. The rate and performance, so production capacity, turned out to be increasing. It is not too much to say that the manufacturing skill of long-length coated conductor for applications reached practical level in this 5 years development.
3. Supply of RE123 coated conductor for power applications

For electric power applications, it is necessary to make the coated conductor into the stable conductor structure by stabilizing and insulating. Metal tape is laminated for stabilization with Sn solder by the reel-to-reel continuous laminating system after sputtering 10 μm thick Ag layer and annealing. The rate of lamination possibly reaches 100 m/h. Figure 17 shows the cross-sectional image of RE123 coated conductor in the across-the-width direction after laminating Cu. For motors and transformers, a Cu tape is laminated to further stabilize the coated conductors. For fault current limiters, a Ni alloy tape with a high resistance is laminated since they are the applications that utilize the difference of resistance when the coated conductors transit from the superconducting state to the normal state. Figure 18 shows the photograph of RE123 coated conductor after final insulating. We wrap a polyimide tape around it for insulating. The supply of RE123 coated conductors fabricated by IBAD/PLD technique in fiscal 2007 is shown in Fig. 19. We supplied total about 4.8 km of RE123 coated conductors for applications after turning into practical usage structures\(^9\).

4. Strategy for the further speed-up

4.1 Further speed-up on IBAD process

In the case of IBAD/PLD technique, IBAD-GZO makes up 50% of total cost. It is necessary to speed up the IBAD process in order to lower the cost of IBAD buffer layer. We are now developing the IBAD buffer layer using MgO, which is reported to exhibit sharp in-plane texture at only several tens nanometers.

Y₂O₃, which is reported to assist the in-plane texture of MgO was laminated on the Hastelloy tape and then MgO layer was grown by IBAD technique on its Y₂O₃ substrate. As a result, 2 types of MgO layer of which the different crystal axis looked toward the normal direction of the substrate turned out to be appear according to the current density of assisting beam and the deposition rate of particle. Figure 20 shows the MgO(200) pole figures of 2 types of IBAD-MgO layer. It indicated that MgO<111> or MgO<100> looked toward the normal direction of substrate.

In the case of the former one, it was necessary to convert the 3 fold symmetry of MgO<111> into the 4 fold symmetry in order to match the RE123 crystals. We therefore grew the conventional GZO layer by IBAD technique on the MgO layer with the 3 fold symmetry, resulting in conversion into the 4 fold symmetry. Figure 21 shows the TEM dark field images of IBAD-GZO layer grown respectively on conventional Hastelloy and on IBAD-MgO layer with the 3 fold symmetry. The part with the white contrast corresponds to the textured part. Hence, these results indicated that
IBAD-GZO layer on IBAD-MgO layer with 3 fold symmetry grows well textured at about one fifth thickness of conventional IBAD-GZO on Hastelloy. In other words, the rate of 25 m/h will be possible, while the conventional rate is 5 m/h. This is our unique buffer structure. We tried to fabricate 1.5 m-length buffer layer with this structure, resulting in well textured IBAD-GZO layer with $\Delta \phi = 13^\circ$ of both ends. In-plane texture reached $\Delta \phi = 4^\circ$ after growing CeO$_2$ layer on this substrate conventionally by PLD technique, resulting in successful growth of GdBCO layer with $I_c$ of about 200 A.

In the case of the MgO<100> type, on the other hand, further high rate than former 3 fold symmetry one can be expected. However, it is critical that the condition of MgO<100> growth is extremely narrow. We are now exploring the optimal condition by the large IBAD system and are able to grow IBAD-MgO buffer layer with good in-plane texture of $\Delta \phi = 10 - 20^\circ$ at the extra high rate of 100 m/h. We are now using only 1 lane, so multi-lane deposition makes it possible to further high rate, which indicates dramatic cost-down.

4. 2 Further speed-up on PLD process

The stable crystal growth at high laser power especially at high frequency without degrading the quality of the crystal is the key point of speed-up in PLD technique. In the case of growing CeO$_2$, we recently succeeded in the stable growth at maximum laser frequency of 300 Hz without degrading in-plane texture by some improvements of laser scanning and so on. As a result, the growth at the rate of 20 - 30 m/h comes to be possible. We also succeeded in speed-up of the GdBCO growth in the same way. We explored the optimal condition on our unique large PLD system with hot-wall heating as shown in Fig. 22, resulting in successful fabrication of long-length GdBCO layer with $I_c$ of over 300 A at the rate of 20 m/h. Further speed-up induced by the improvement of critical current density $J_c$ is now being tried.

5. Conclusion

Developments of RE123 coated conductors by IBAD/PLD technique have steadily progressed and
we succeeded in the fabrication of 500 m-length one with $I_c$ of over 300 A at last in Feb. 2008. $I_c\cdot L$ value exhibited world record performance and reached practical level. In accordance with these progress, verification test of power electric applications using these coated conductors has also started. It is not too much to say that applications using these coated conductors will appear on actual market near future. We are due to promote the development for mass production by increasing the production rate and decreasing the cost furthermore.

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