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# Fabrication of Sm123 film on Ni textured substrate by PLD method

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We fabricated Sm123 films by PLD on the textured Ni substrate. A $BaZrO_3$ film is adopted as a buffer layer on the metal substrate because the $BaZrO_3$ has a significant effect improving the crystal grain in-plane alignment of the Sm123 grains. The in-plane grain alignment of an NiO layer grown by annealing the Ni substrate was, however, worse compared with that of Ni substrate.

We tried to improve the Surface Oxidation Epitaxy (SOE) process. Conventionally, Ni substrates were annealed at high temperature and in a high oxygen partial pressure atmosphere. In this study, the annealing process is made into two separate stages, the first annealing in a low oxygen atmosphere followed by the conventional annealing. A good NiO film was obtained by forming a good in-plane grain alignment film in the first stage of oxidation.

Key words: Sm123, SOE, $BaZrO_3$, buffer layer, PLD

## 1. INTRODUCTION

We have tried to fabricate Sm123 films by PLD on textured SOE-Ni substrates since Sm123 has higher Tc value than that of Y123 and high Jc-B properties are expected especially in high magnetic fields. To obtain the high superconductivity properties, we have to form a good in-plane alignment film of the Sm123. However, the in-plane grain alignment of an NiO layer grown by annealing the Ni substrate was worse compared with that of Ni substrate. We have to be fabricated the highly textured SOE. In this study, the improvement of the texturing in the SOE has been investigated.

## 2. EXPERIMENTAL

In order to investigate the effects of $Po_2$ and the temperature in the SOE process, the following different conditions were used in this study;

The temperature and $Po_2$ used in this study for annealing to form the NiO are listed in Table 1. In this table, the annealing condition of 1100℃ and $Po_2$ =$2.1\times10^{4}$Pa is the conventional SOE condition. Next, the substrates annealed at 750℃ under $Po_2$ of $5\times10^{-2}$Pa were annealed at 1000℃ to 1200℃ for several hours in Air to obtain thick NiO layer as the second annealing. The $BaZrO_3$ and Sm123 were grown on the annealed substrates by the Pulsed laser deposition (PLD) method after polishing the surface mechanically.

The cross-sectional views of the prepared samples were observed by optical microscopy and the grain alignments of the samples were analyzed by XRD. The values of *Tc* and *Jc* were measured by the conventional 4-probe method after annealing at 350℃ for an hour in flowing oxygen.

## 3. RESULTS AND DISCUSSION

Table 1 shows the influence of the temperature and $Po_2$ on the texturing of the NiO layer. As shown in the table, the low $\Delta\phi$ values could be recognized in the films annealed under low $Po_2$ conditions at both temperatures.

Table 1 NiO formed by first annealing

| Temperature | $Po_2$ | $\Delta\phi$ | I(200)/ΣI(hkl) | Thickness |
|---|---|---|---|---|
| 1100℃ | $2.1\times10^{4}$Pa | 15.0% | 89.5% | 13.7μm |
| 1100℃ | $5\times10^{-2}$Pa | 7.5% | 100% | <1μm |
| 750℃ | $2.1\times10^{4}$Pa | 19.3% | 79.4% | 7.5μm |
| 750℃ | $5\times10^{-2}$Pa | 7.1% | 100% | <1μm |

This means that the $Po_2$ is a dominant factor to determine the texturing of NiO layer.

Hence, we investigate the effect of $Po_2$ for the oxidation of Ni. The reaction of oxidation of Ni is expressed as follows,

$$<\mathrm{Ni}>+\frac{1}{2}\{\mathrm{O_2}\}\rightarrow<\mathrm{NiO}> \qquad (1)$$

The free energy change for this reaction, $\Delta G$, is expressed by the following formula,

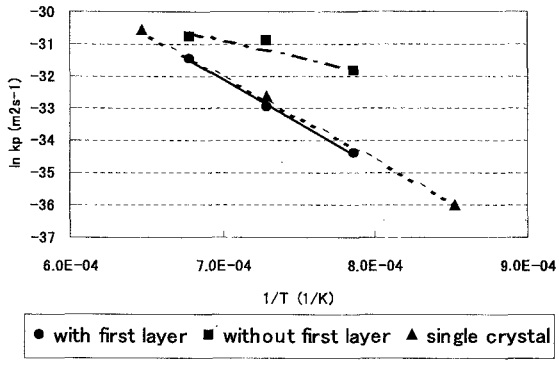


Fig. 3 Temperature dependence of rate constant.

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{a_{NiO}}{a_{Ni} Po_2^{\frac{1}{2}}} \tag{2}$$

where $\Delta G^{\circ}$ is the standard free energy change for NiO formation, $a_{NiO}$ and $a_{Ni}$ are activities of NiO and Ni, both could be considered to be unity because both phases are pure solid materials. Therefore, the equation(2) can be simplified as,

$$\Delta G = \Delta G^{\circ} + RT \ln Po_2^{-\frac{1}{2}} \tag{3}$$

Here, the free energy change can be obtained using equilibrium condition of $\Delta G=0$. Here, the further simplified expression can be derived by the $\Delta G^{\circ}$ and Eq. (3) as,

$$\Delta G = -\frac{1}{2} RT \ln \frac{Po_2}{Po_2^*} \tag{4}$$

where $Po_2^*$ is the equilibrium partial pressure of oxygen vapor. The ratio of $Po_2$ and $Po_2^*$ is defined as the surpersaturation of the oxygen, $\sigma$, as,

$$\sigma \equiv \frac{Po_2}{Po_2^*} \tag{5}$$

As shown in Table 2, the values of $\sigma$ and $\Delta G$ at 1100℃ were calculated by Eqs. (4) and (5) using the $Po_2^*$ value of $5.4\times10^{-4}$Pa, which was obtained from the $\Delta G^{\circ}$ equation,

$$\Delta G^{\circ} = RT \ln Po_2^{*\frac{1}{2}} \tag{6}$$

From this table, the low driving force for the formation of the NiO in the low $Po_2$ condition can be confirmed.

Table 2 Driving force for NiO formation depended on at 1000℃

| $Po_2$ | $2.1\times10^{4}$Pa | $5\times10^{-2}$Pa |
|---|---|---|
| $\sigma$ | $3.8\times10^{7}$ | 92 |
| $\Delta G$ | -100kJ/mol | -24kJ/mol |

We consider the influence of $\sigma$ on the grain alignment of the NiO grains. The free energy change for the nucleation is expressed as follows,

$$\Delta G_{necleus} = V\Delta Gv + A\gamma + A'\gamma' \tag{7}$$

where V is a unit cell volume, $\Delta Gv(=\Delta G/V_{NiO})$ is volumetric free energy change, $\gamma$ is interfacial energy between NiO and Ni, and $\gamma'$ is surface energy of NiO. The nucleation frequency, $I$, is expressed using $\Delta G_{nucleus}$ as follows,

$$I = B\exp(\frac{\Delta G_{necleus}}{kT}) \tag{8}$$

The $\gamma$ value strongly depends on the alignment of the embrio on the substrate, although the $\gamma'$ is independent. In the small $\sigma$ region, the $I$ curve with small $\gamma$ can only represent a finite value as shown in fig. 1. This means that well aligned grains are selectively formed. On the other hand, the grains of larger $\gamma$, which have worse grain alignment with the substrate, can be nucleated. From the above discussion, it can be concluded that a highly textured structure in the low $Po_2$ condition can be formed by the selective nucleation of the aligned grains due to the small supersaturation.

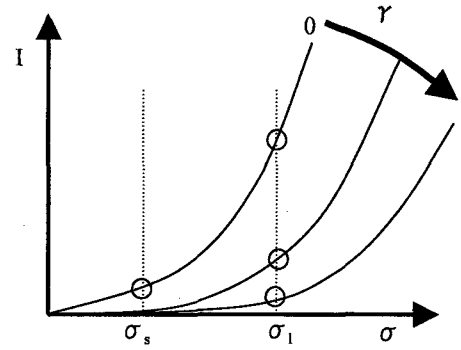


Fig. 1 Schematic figure the relation between supersaturation and nucleus rate.

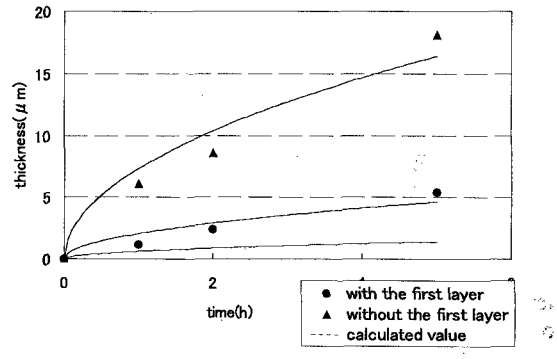


Fig. 2 Time dependence of thickness

Next, we investigated the effects of the first layer grown in low $Po_2$ on the further growth in the second annealing. An Ni textured substrate with an NiO layer grown in low $Po_2$ (with the first layer) and Ni textured substrate (without the first layer) were annealed under high $Po_2$ of $2\times10^{-4}$Pa at the different temperatures. Figure 2 shows the time dependence of the NiO thickness at 1000℃. The dashed line shows the value calculated from the volumetric diffusion coefficient of

Ni. When oxidizing the Ni at the high temperature, the time dependency of the thickness is shown a parabolic law as shown in the following formula,

$$x = \sqrt{k_p t} \tag{9}$$

where $k_p$ is a rate constant, t is the annealing time, x is thickness.
The $k_p$ values could be obtained from Fig. 3 and Eq. 9 as shown in Table 3.

Table 3 Rate constant at 1000℃

| | without the first layer | with the first layer | from calculated value |
|---|---|---|---|
| $k_p(m^2s^{-1})$ | $1.5\times10^{-14}$ | $1.2\times10^{-15}$ | $1.1\times10^{-16}$ |

The $k_p$ value of the sample with the first layer is smaller than that without the first layer. However, it is still larger than that calculated by the volumetric diffusivity. This means that the effect of diffusion along the grain boundaries, which is higher than that in the grain, can not be neglected even in the sample with the first layer and the effect is stronger in the sample without the first layer.
Figure 3 shows the temperature dependence of $k_p$.
The dashed line showed the $k_p$ values of NiO single crystals reported by Graham [2]. The data of the oxidation with the first layer is equivalent with of single crystals. The activation energy, *Ea*, could be calculated from the gradient of the lines.

Table 4 Activation energy for oxidation at 1000℃

| | without the first layer | with the first layer | single crystals |
|---|---|---|---|
| *Ea* (kJ/mol) | 5 | 13 | 13 |

The small Ea value in the sample without the first layer might be due to diffusion along the grain boundaries.
The relation between the thickness of the NiO and $\Delta\phi$ is shown in fig. 4. The $\Delta\phi$ value of the sample without the first layer increases with increasing the thickness of the NiO, although that is maintained even in the thick film for the sample with the first layer. The pole figures of the NiO formed by the two-step annealing and Sm123 grown on it are shown in fig. 5.

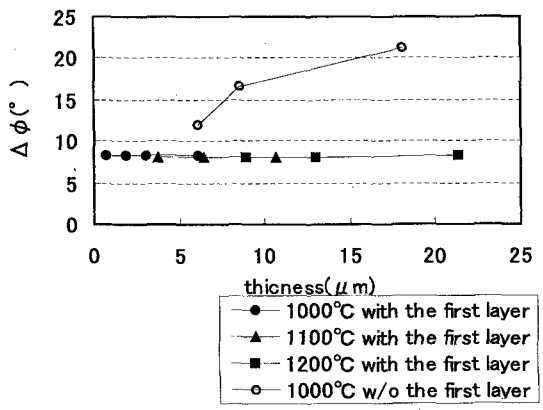


Fig. 4 Relation between the thickness of NiO and $\Delta\phi$.

The in-plane grain alignment of the NiO was improved resulted in high *Tc* and *Ic* values of 91.7K and 120A, respectively.

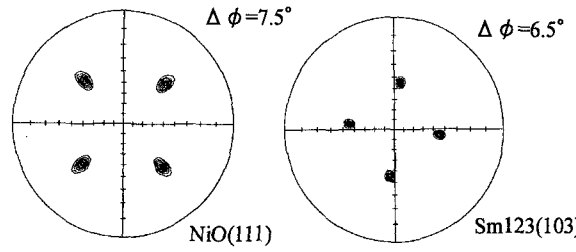


Fig. 5 Pole figures of NiO and Sm123

## 4. CONCLUSION

Through the investigation of the influence of $Po_2$ and the temperature for formation of NiO layer, it was found that the effect of $Po_2$ was dominant factor to determine the texturing of the NiO layer. The texturing of the first NiO layer affects the successive growth in the high $Po_2$ condition. Using the highly textured NiO with a reasonable thickness by the two-step annealing, the Sm123/$BaZrO_3$ film fabricated on the textured SOE showed *Tc*=91.7K and *Ic*=120A.

## 5. Acknowledgement

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