Basic Study for Formation of BiSrCaCuO Thin Film by Molecular Beam Epitaxy

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Bi and Cu oxidation using pure ozone (O₃) was investigated for in situ synthesis of BiSrCaCuO superconducting thin film. Threshold-like behaviour of ozone partial pressure at substrate surface (Pₐₖ) for Bi incorporation into the film and CuO formation is demonstrated. Above threshold of Pₐₖ for oxidation of Bi and Cu, BiSrCaCuO superconducting film was synthesized in situ by molecular beam epitaxy method and complete superconducting transition was obtained at ~63K without any annealing steps.

1. INTRODUCTION

In order to synthesize oxide superconducting thin film by molecular beam epitaxy (MBE) method, a oxygen gas source having strong oxidation power is desired to use. Recently BiSrCaCuO superconducting thin film was synthesized in situ by MBE method using pure ozone (13-21). MBE method is one of the promising methods for atomic layer epitaxy and for in situ observation of crystal growth by electron spectroscopy (22). Molecular beam epitaxial process of BiSrCaCuO superconducting crystal structure was investigated using pure ozone and nitrogen dioxide (22-31). However, as far as oxidation of metal elements is concerned, it does not seem to study sufficiently. In this study, we focused on Bi and Cu oxidation behaviour of ozone for in situ growth of BiSrCaCuO superconducting thin films. In situ synthesis of BiSrCaCuO superconducting thin film using pure ozone is also demonstrated.

2. Experimental

Bi incorporation into the BiSrCaCuO thin film is expected to depend on oxidation of Bi, because vapour pressure of Bi₂O₃ is considerably smaller than that of Bi at given temperature. From this point of view, Bi oxidation can be examined to some extent by measuring Bi composition of the BiSrCaCuO thin film as a function of substrate temperature (Tₛ) and ozone partial pressure at substrate surface (Pₐₖ). Composition of BiSrCaCuO formed on MgO(100) substrate at various Tₛ and Pₐₖ were analyzed by energy dispersive X-ray (EDX).

It is expected that Pₐₖ depends on position (d) on substrate surface due to cosθ distribution of ozone from the gas nozzle. Then Bi composition as a function of d along a line was also measured.
In order to examine oxidation of Cu using ozone as a function of \( P_{O_3} \) and \( T_s \). Cu was deposited on MgO(100) substrate under various \( P_{O_3} \) and \( T_s \) conditions in the MBE growth chamber. CuO and Cu\(_2\)O formation was identified by X-ray diffraction (XRD) analysis.

Pure ozone was generated by the similar apparatus of Berkley's \(^1\). 5% ozone was concentrated to pure ozone in the still cooled by liquid nitrogen. Pure ozone was introduced onto the substrate with the gas nozzle. \( P_{O_3} \) was adjusted by temperature control at the still.

BiSrCaCuO superconducting thin film was synthesized on MgO(100) substrate by MBE method using pure ozone at \( T_s \sim 700^\circ\). Metal source of Bi, Sr, Ca and Cu were coevaporated. Back ground pressure was \( 6 \times 10^{-5} \) Torr during film growth. Temperature dependence of resistivity was measured by the standard four point probe method.

3. Results

Fig. 1 (a) shows ratio of Bi composition to Sr (Bi/Sr) as a function of \( P_{O_3} \) for the BiSrCaCuO thin film formed at \( T_s \sim 700^\circ\). \( P_{O_3} \) was estimated assuming \( \cos^2\theta \) distribution of ozone from the gas nozzle. Bi/Sr decreases rapidly at \( P_{O_3} \sim 3 \times 10^{-5} \) Torr. Threshold-like behaviour of \( P_{O_3} \) for Bi incorporation or Bi oxidation was also observed in Bi composition of the thin film as a function of \( d \) (Fig. 1(b)); this film was synthesized at \( T_s \sim 550^\circ\) and background pressure \( 8 \times 10^{-6} \) Torr. Bi decreases rapidly at a certain position (\( d = d_{th} \)). In this case, \( P_{O_3}(d = d_{th}) \sim 5 \times 10^{-6} \) Torr. Fig. 1(c) shows Bi/Sr as a function of \( T_s \) at \( P_{O_3} \sim 2.4 \times 10^{-4} \) Torr and Bi/Sr decreases rapidly at \( T_s \geq 700^\circ\); threshold of \( T_s \) for Bi incorporation was \( T_s \sim 760^\circ\). Ozone is also spent to oxidize Sr, Ca and Cu, which results in higher threshold of \( P_{O_3} \) for Bi oxidation than as it is.

The boundary between CuO and Cu\(_2\)O formation was also clearly observed on Cu oxide thin film. This implies that there exists threshold of \( P_{O_3} \) for CuO formation. Fig. 2 shows the diagram for CuO and Cu\(_2\)O formation as a function of \( P_{O_3} \) and \( T_s \). The solid line indicates the boundary between CuO and Cu\(_2\)O formation.

In order to synthesize the superconducting thin film in situ, \( P_{O_3} \) is desired to be at least larger than threshold of \( P_{O_3} \) for Bi incorporation and CuO formation. Fig. 3 shows
temperature dependence of resistivity of the BiSrCaCuO thin film; it was synthesized by MBE method using pure ozone whose partial pressure was larger than threshold. Growth conditions are indicated in Table 1. Stoichiometric composition of the thin film was 2:2:1:2. Onset and complete superconducting transition were obtained at \(-100\) K and \(-65\) K, respectively. Temperature at complete superconducting transition is still low and further analysis is required to clarify this reason.
Table 1 Growth conditions for the BiSrCaCuO superconducting thin film

<table>
<thead>
<tr>
<th>Temperature of source furnaces</th>
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<tr>
<td>Bi</td>
<td>510°C</td>
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<tr>
<td>Sr</td>
<td>465°C</td>
</tr>
<tr>
<td>Ca</td>
<td>450°C</td>
</tr>
<tr>
<td>Cu</td>
<td>980°C</td>
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Background pressure of the growth chamber
6x10^-5 Torr (O_3 feeding)

Substrate
MgO(100); T_s~ 700 °C

4. Summary

Bi and Cu oxidation behaviour of ozone were systematically examined. It is demonstrated that there exists threshold of P_{O_3} for oxidation of Bi and Cu. Above threshold of P_{O_3} for Bi and Cu oxidation, BiSrCaCuO superconducting thin film was synthesized by MBE method using pure ozone; complete superconducting transition was obtained at ~65 K without any annealing steps.

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References