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

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Bi and Cu oxidation using pure ozone (O_3) was investigated for in situ synthesis of BiSrCaCuO superconducting thin film. Threshold-like behaviour of ozone partial pressure at substrate surface (P_{O3}) for Bi incorporation into the film and CuO formation is demonstrated. Above threshold of P_{O3} 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 ~65K 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. Resently BiSrCaCuO superconducting thin film was synthesized in situ by MBE method using pure ozone [1)-2)]. MBE method is one of the promissing methods for atomic layer epitaxy and for in situ observation of crystal growth by electron spectroscopy [2)]. Molecular beam epitaxial process of BiSrCaCuO superconducting crystal structure was investigated using pure ozone and nitrogen deoxide [2)-3)]. 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 sysnthesis 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 Bi_2O_3 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 (T_S) and ozone partial pressure at substrate surface (P_{O3}). Composition of BiSrCaCuO formed on MgO(100) substrate at various T_S and P_{O3} were analyzed by energy dispersive X-ray (EDX) .

It is expected that P_{O3} depends on position (d) on substrate surface due to $\cos^n\theta$ distribution of ozone from the gas nozzle. Then Bi composition as a function of d along a line was also measured.

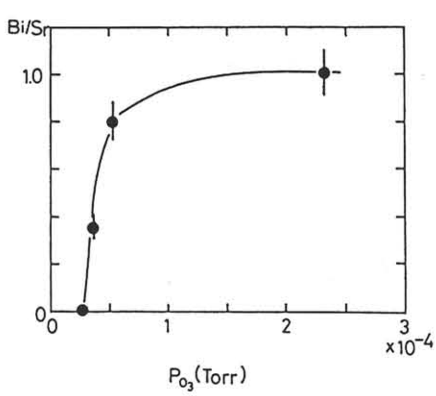
In order to examine oxidation of Cu using ozone as a function of P_{O_3} and T_S. Cu was deposited on MgO(100) substrate under various P_{O_3} and T_S conditions in the MBE growth chamber. CuO and Cu_2O formation was identified by X-ray diffraction (XRD) analysis.

Pure ozone was generated by the similar apparatus of Berkley's [4]. 5% ozone was consentrated 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 controle at the still.

BiSrCaCuO superconducting thin film was synthesized on MgO(100) substrate by MBE method using pure ozone at T_S~700℃. Metal source of Bi, Sr, Ca and Cu were coevaporated. Back ground pressure was 6×10^{-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~700℃. P_{O_3} was estimated assuming $\cos^n\theta$ distribution of ozone from the gas nozzle. Bi/Sr decreases rapidly at P_{O_3}~3×10^{-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~550℃ and backgroung pressure~8×10^{-6} Torr. Bi decreases rapidly at a certain position ($d=d_{th}$). In this case, $P_{O_3}(d=d_{th})$~5×10^{-6} Torr. Fig. 1(c) shows Bi/Sr as a function of T_S at P_{O_3}~2.4×10^{-4} Torr and Bi/Sr decreases rapidly at $T_S \geqq 700$℃; threshold of T_S for Bi incorporation was T_S~760℃. 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.



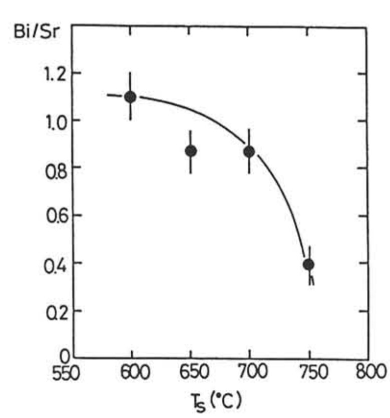


Fig.1(a) Bi/Sr as a function of ozone partial pressure at substrate surface P_{O_3} at Ts~700℃.

Fig.1(c) Bi/Sr as a function of T_S at P_{O_3}~2.4×10^{-4} Torr.

The boundary between CuO and Cu_2O 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_2O formation as a function of P_{O_3} and T_S. The solid line indicates the boundary between CuO and Cu_2O 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

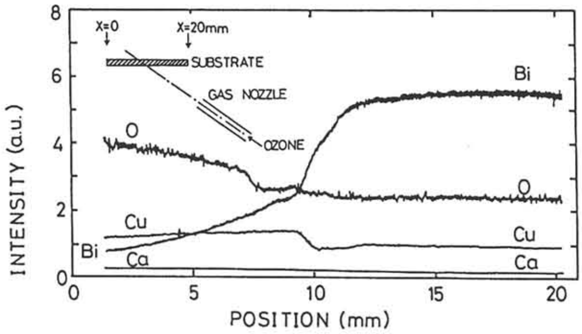


Fig.1(b) Bi composition of the BiSrCaCuO thin film as a function of position on substrate surface.

temperature dependence of resistivity of the BiSrCaCuO thin film; it was sysntesized 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.

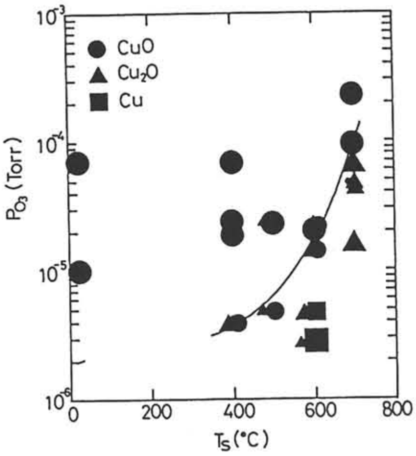


Fig.2 Phase diagram for CuO and Cu_2O formation as a function of P_{O_3} and T_S. The solid line indicates guide to the eye for the boundary between CuO and Cu_2O formation.

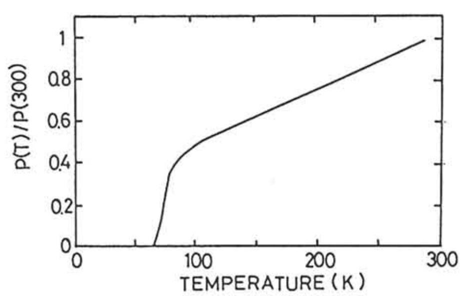


Fig.3 Temperature dependence of resistivity of the BiSrCaCuO superconducting thin film.

Table 1 Growth conditions for the BiSrCaCuO superconducting thin film

Temperature of source furnaces		
	Bi	510℃
	Sr	465℃
	Ca	450℃
	Cu	980℃
Background pressure of the growth chamber		
6×10^{-5} Torr (O_3 feeding)		
Substrate		
MgO(100) ; $T_S\sim$ 700 ℃		

4.Summery

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.

Acknoledgement

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