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Design of Layered Structure in the High Tc Oxide Superconducting Thin Films with Layer-by-Layer Successive Deposition

Tomoji KAWAI
ISIR, Osaka University, Mihogaoka, Ibaraki, Osaka 567 Japan

By using layer-by-layer successive deposition method utilizing excimer laser ablation, the CuO_2 based structures in high Tc superconducting oxides have been controlled and superlattices have been formed. These tailored films have shown that there is an interaction between CuO_2 planes across mediating layers, such as Ca or Y, while there is a very weak interaction across blocking layers, such as $SrO/Bi_2O_2/SrO$ layer.

1. INTRODUCTION

The essential structural feature of high-Tc cuprates is CuO_2 layers doped with charge carriers. The infinitely stacked CuO_2 layers are separated by blocking layers and mediating layers to form the two dimensional layered structure.(Fig.1) Here, the blocking layers include layers of rock salt(LaO, SrO etc.), Bi_2O_2, Tl_2O_2, fluorite(Nd_2O_2 etc.), PbO and CuO chains, and mediating layers include small cations, such as Ca^{2+} and Y^{3+}. Any of the superconductors so far discovered can be classified by the combination of these blocking layers and mediating layers.

In order to control the superconductivity, we should control the unit of CuO_2-based structure sandwiched by blocking layers, that is, the number of CuO_2 layers, spacing between CuO_2 layers and Cu-O bond length. These structures can be changed by choosing appropriate combination of blocking and mediating layers and by the incorporation of exotic ions with different ionic radii above, below or between the CuO_2 layers. The formation of these "Tailored thin films" have been carried out by using layer-by-layer successive deposition method.

From the crystallographic point of view, this layer-by-layer method can be applied to the control of the composition across the different unit cells. We are able to form superlattices by modulating concentration and composition across each unit cell layer.

We summarize here our recent works on "layer-by-layer successive deposition method using laser ablation" for the control of the structure and also for the formation of superlattices in the "Tailored Superconducting Films." From these experiments, we argue that the interaction across blocking layers is very weak and that across mediating layers is strong and important to determine the Tc value.

2. EXPERIMENTAL

The apparatus used for the film formation is shown in Fig.2.[1,2,3] The emitted atoms and molecules by the ablation are accumulated on an MgO(100) or $SrTiO_3$(100) substrate placed at the opposite side of the targets. The emitted atoms and ions are monitored in situ by mass spectrometer. The laser beam is split into two beams, one for the ablation and the other for the substrate excitation.

For the layer-by-layer successive deposition, an ArF laser beam is sequentially focused on multi-targets to form thin layers successively on the substrate in the presence of O_2 and N_2O mixture or in NO_2 atmosphere. For the successive deposition of Bi-Sr-Ca-Cu-O system, for example, sintered disks of $Bi_{1-x}Pb_xO_y$, SrCuOy, CaCuOy and/or disks containing other cations are used as targets, and each different layer is successively deposited from these targets to form multi-layered structure as we desire. One cycle to form one Bi-Sr-Ca-Cu-O layer consists of the sequence of the deposition from the targets, for example, Bi(Pb)Oy-SrCuOy-CaCuOy-SrCuOy for the standard $Bi_2Sr_2Ca_1Cu_2O_y$ film, and this cycle is repeated 20 to 40 times to form a film thickness of about 300 to 600A. The structures are identified by RHEED in situ, and compositions are determined by AES.

3. RESULTS AND DISCUSSION

(3-1) Control of the spacing between CuO_2 planes.

For the control of the distance between CuO_2 planes in the $Bi_2Sr_2Ca_1Cu_2O_8$, for example, atoms having different ionic radii should be incorporated into the Ca site of BSCCO. We have examined the incorporation of Ba, Sr and Mg, the large or small +2 ion, into the Ca sites of BSCCO using layer-by-layer successive deposition.[2] In this experiments, Ba, Sr or Mg atom is co-deposited when $CaCuO_2$ layer is formed during the successive deposition. With this method, Ba, Sr, or Mg is actually introduced into the structure, judged from the X-ray diffraction patterns of single $Bi_2Sr_2Ca_1Cu_2O_8$ phase and by EPMA measurement as reported previously[2].

The transition temperatures and lattice paramenters of the substituted samples for the Ca site are measured. The change of

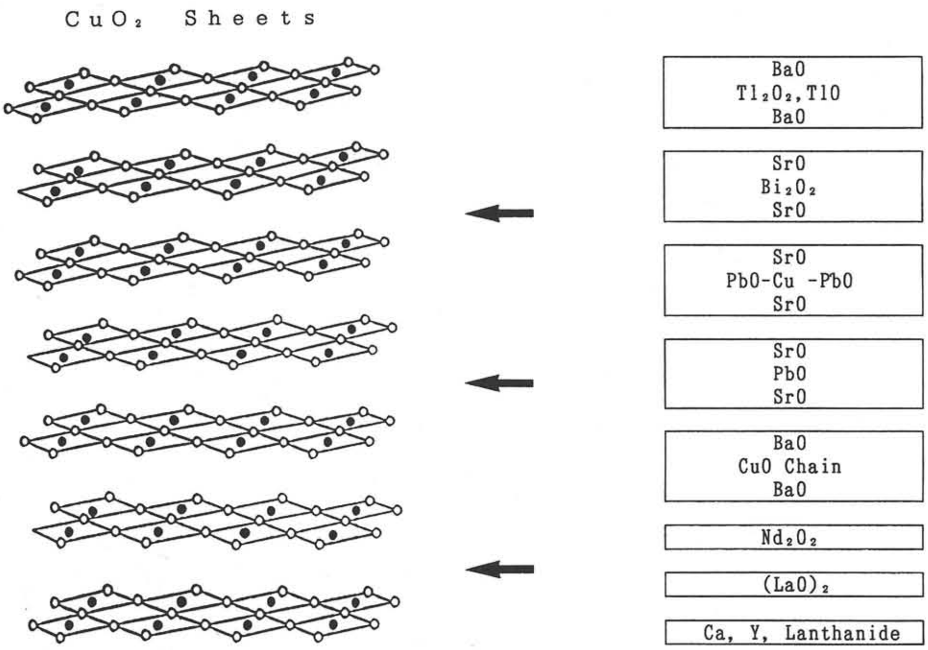

Fig.1 Schematic representation of Cu based superconductors

the Tc against the ionic radii for the incorporation of Mg, Sr and Ba at the Ca site indicates that the spacing between CuO_2 layers is one of the important determining parameters for the Tc value and that larger spacing with expansion of the c-axis makes higher Tc. These results indicate that there is a strong interaction between CuO_2 layers to affect the Tc value. In this sense, the Ca layer in BSCCO and Y layer in $YBa_2Cu_3O_7$ should be called as a mediating layer.

(3-2) New combination of unit cell layers: the superconducting superlattice

In order to know the interaction across the blocking layer, such as Bi_2O_2, superlattices consisting of superconducting/ semiconducting layers are effective. We have fomed the superlattices consisting of the combination of the unit cell layers of $Bi_2Sr_2Ca_1Cu_2O_8/Bi_2Sr_2Cu_1O_6$ (2212/2201 superlattice) and the combination of $Bi_2Sr_2(Ca_{0.85}Y_{0.15})Cu_2O_y$ (Y:15%, semiconductor) and $Bi_2Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_y$ (Y:50%, semiconductor).[3] For the 2212/2201 superlattices, satellite peaks due to the superlattice formation are observed. For the series of Y(15%)/Y(50%) superlattices, the numbers of the stacking of each layer are varied to 8:4, 4:2 and 2:1, which makes the average compositon of $Bi_2Sr_2(Ca_{0.75}Y_{0.25})Cu_2O_y$(Y:25%) that is semiconductor. Even though the numbers of Y(15%)-unit cell layer are decreased from 8 to 2, keeping the ratio to the number of the Y(50%) layer to be 2:1, Tc is similar to that of the original Y(15%) compound. This may indicate that there is no inter-diffusion of Y between two different $Bi_2Sr_2(Ca_{1-x}Y_x)Cu_2O_y$ unit cells during the film formation to randomize charge carriers, and also there is only a very weak interaction to affect the superconductivity across the $SrO/Bi_2O_2/SrO$ blocking layers. In this sense, these Bi_2O_2 and SrO layers can be called "blocking layers".

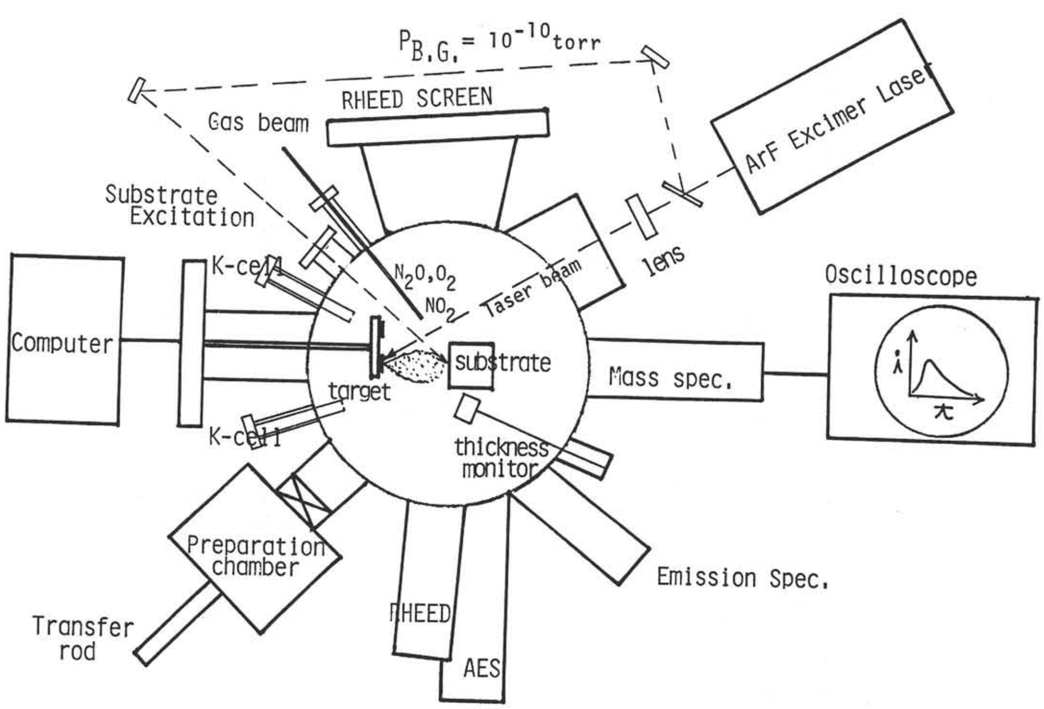

Fig.2 Apparatus for Laser MBE

In conclusion, structural parameters based on CuO_2 planes are changed artificially, constructing the films layer-by-layer using laser ablation. The superconductivity of the artificial films can be controlled by changing these structures. This technique to fabricate "Tailored Superconducting Films" seems to be quite useful to elucidate the superconductivity mechanism. It has been suggested that there is a strong interaction between CuO_2 layers inside of the blocking layers, but there is quite weak interactions across the blocking layers, such as Bi_2O_2. The superconductivity seems to appear within the two dimensional CuO_2 layers having strong interactions sandwiched by blocking layers.

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