MBE Growth and Element-distinctive Atomic-resolution Characterization of High Temperature Superconductors

Ai Ikeda, Yoshiharu Krockenberger, Yoshitaka Taniyasu, and Hideki Yamamoto

Abstract

Cuprate superconductors are in the material family that have the highest superconducting transition temperature (T_c) of ~130 K under ambient pressure. The infinite-layer structure is the essential building block of high-T_c cuprates with a T_c of over 100 K and is therefore vital to understand the mechanism of high-T_c superconductivity. While the infinite-layer phase is inaccessible using bulk single-crystal synthesis methods, we synthesized single-crystalline thin films of the infinite-layer cuprates using our unique oxide molecular beam epitaxy setup. To clarify the relationship between their microscopic crystal structures and electronic responses, we performed atomic-resolution electron microscopy measurements of the CuO_2 (copper peroxide) planes in the infinite-layer cuprates, the playground of high-T_c superconductivity.

Keywords: superconductivity, oxide molecular beam epitaxy, scanning transmission electron microscopy

1. Introduction

Superconductivity is a phenomenon in quantum materials that allows for lossless transportation of electrical current, and thus of energy and information. The quantum phenomenon, superconductivity, had been observed only below –140°C (~130 K) until very recent reports on hydrides, that is, sulfur hydride (H_3S) and lanthanum hydride (LaH_{10}). These materials show significantly higher superconducting transition temperatures (T_cs): –70°C (~200 K) for H_3S [1] and even close to room temperature for LaH_{10} [2]. Synthesizing these hydrides, however, requires extremely high pressure, specifically, ~2 million times higher (~200 GPa) than the atmospheric pressure. To make matters more complicated, their crystal structures are altered when the pressure is reduced after synthesis. In other words, the superconducting phases can exist only under an extremely high pressure comparable to that at the core of the Earth. Accordingly, practical applications using these hydrides remain elusive despite the significance of their discoveries from an academic point of view.

In contrast, cuprates are superconductors that exhibit the highest T_c under ambient pressure. Among them, $YBa_2Cu_3O_{7-\delta}$ (yttrium barium copper oxide) as well as $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (bismuth strontium calcium copper oxide), both of which show higher T_c (~90 K and ~110 K, respectively) than the boiling point of nitrogen (77 K), have already yielded practical applications as superconducting cables and microwave filters. However, the mechanism of high-T_c superconductivity in cuprates remains unclarified despite immense efforts for over three decades, which has been hampering the strategic search of novel superconducting materials with a higher T_c.
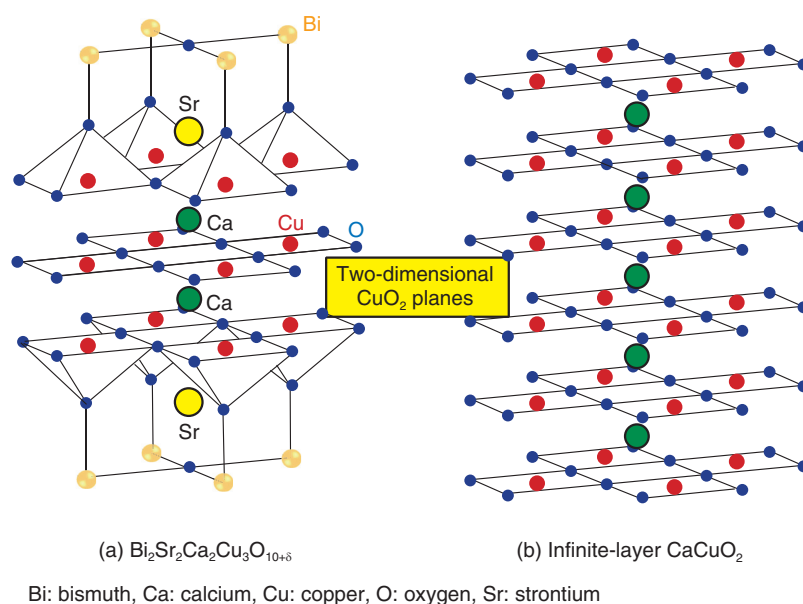
(a) $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (b) Infinite-layer $CaCuO_2$

Bi: bismuth, Ca: calcium, Cu: copper, O: oxygen, Sr: strontium

Fig. 1. Crystal structures of cuprate superconductors.

Nonetheless, the fundamental structural ingredient of high-T_c cuprates is fortunately well known: copper peroxide (CuO_2) planes, as exemplified by $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (**Fig. 1(a)**). Two-dimensional CuO_2 planes are made up of copper (Cu) and oxygen (O) and are separated by bismuth (Bi), strontium (Sr), calcium (Ca), and O. The formal valences of O and Cu are 2– and 2+, respectively, so the CuO_2 plane is not charge-neutral and cannot exist independently. Instead, the minimal structural unit that is compassable is charge-neutral calcium copper oxide ($CaCuO_2$) (**Fig. 1(b)**), which is commonly included in cuprates whose T_cs are above 100 K; the crystal structure shown in Fig. 1(b) is called an infinite-layer structure. That is why we have been focusing our research efforts on infinite-layer cuprates. Because the synthesis of bulk specimens of $CaCuO_2$ requires high pressure levels (3–5 GPa), single-crystalline $CaCuO_2$ specimens can be prepared exclusively by using thin-film growth methods, in our case, molecular beam epitaxy (MBE). Unlike the above-mentioned hydrides, the infinite-layer structure is stable at ambient pressure once it is formed.

2. Fabrication of ultrahigh-quality infinite-layer cuprate superconductors

While MBE has been widely used for the growth of semiconductors, we have extended it to the growth of complex transition metal oxides. Our customized MBE method is well equipped not only to synthesize novel complex transition metal oxides, for example, Sr_3OsO_6, a new ferromagnetic insulator with a Curie temperature > 1000 K [3], but also to push the limits of common crystal growth methods [4], and this is illustrated in **Fig. 2**. The vacuum recipient is 70 cm in diameter and 150 cm in height. A total of 10 metal sources are mounted at the bottom of the vacuum recipient where the elements can be evaporated by electron guns operated at 10 kV. The evaporant flux of each element is monitored and controlled by electron impact emission spectroscopy (EIES). The details of EIES are explained in another article in this issue [5].

Molecular oxygen (O_2) is insufficient for the growth of complex transition metal oxides, and therefore, the oxide MBE system is equipped with stronger oxidizing agents. This is distinct from conventional MBE. In this work, radio-frequency radical oxygen (O) was used for the growth of infinite-layer cuprates. Oxidation/reduction involves the gain/loss of electrons. Radical oxygen has two unpaired electrons and therefore a strong tendency to deprive the neighboring metal atoms of electrons. The absence of kinetic barriers in atomic oxygen is what drives the growth of complex transition metal oxides in an ultrahigh vacuum (~10^{-9} atm). In addition, the growth orientation is defined by the substrate; this phenomenon
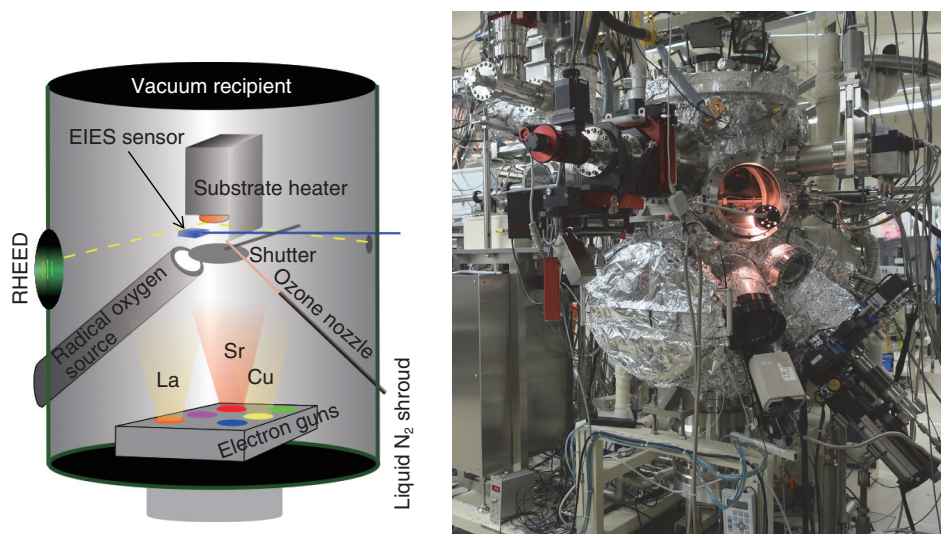
EIES: electron impact emission spectroscopy
La: lanthanum
N$_2$: nitrogen
RHEED: reflection high-energy electron diffraction
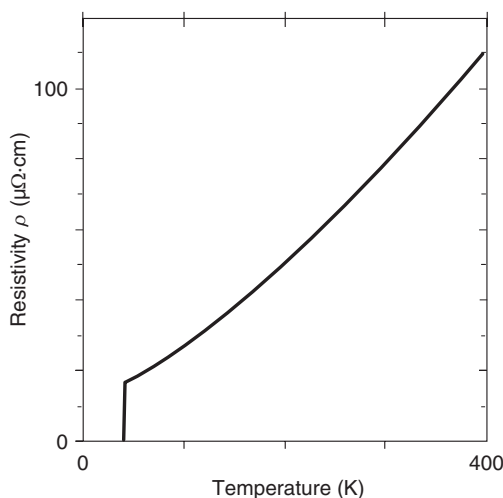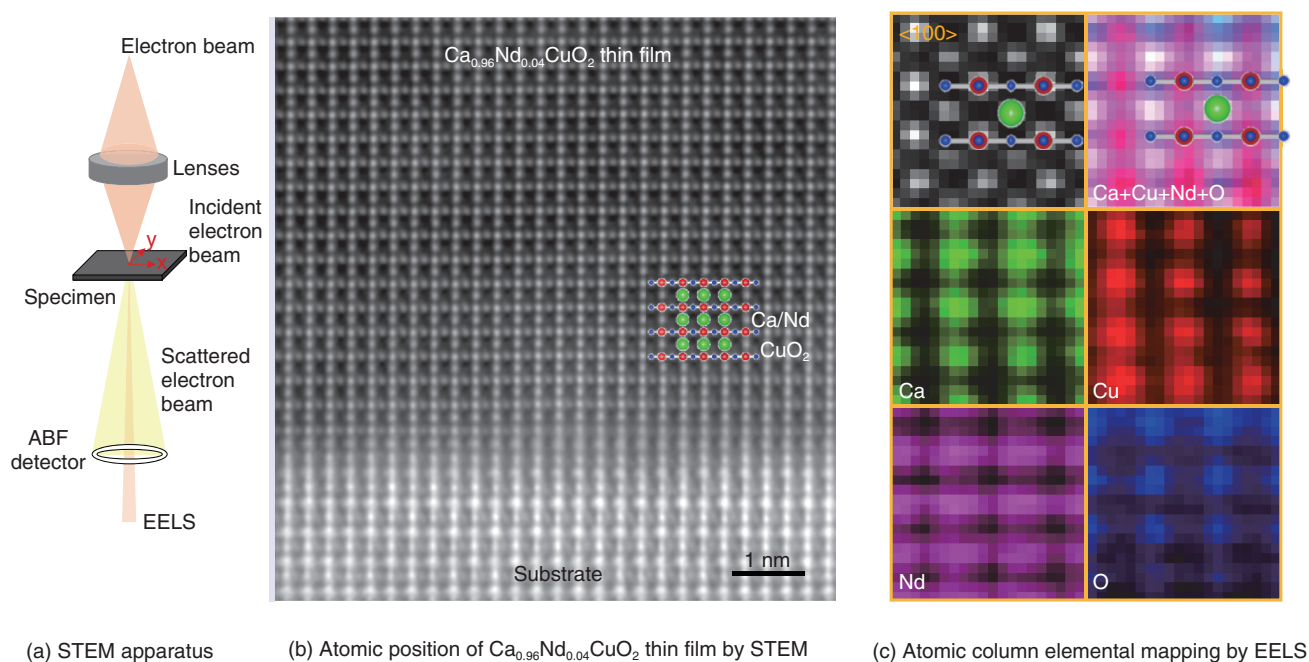
Fig. 2.   Oxide MBE setup.

Fig. 3.   Temperature dependence of resistivity for Sr$_{0.9}$La$_{0.1}$CuO$_2$ thin film.

is called *epitaxy* (in Greek, order on top). We used a single-crystal substrate with a lattice constant closer to one for infinite-layer cuprates. This mechanism enables the formation of single-crystalline infinite-layer cuprates.

We used the oxide MBE system to synthesize superconducting infinite-layer Sr$_{0.9}$La$_{0.1}$CuO$_2$ thin films [6–9]. In Sr$_{0.9}$La$_{0.1}$CuO$_2$, strontium ions (Sr^{2+}

ions) are partially substituted with La^{3+} ions (lanthanum ions) to induce superconductivity. The dependence of resistivity on temperature for the Sr$_{0.9}$La$_{0.1}$CuO$_2$ thin film is plotted in **Fig. 3**. Resistivity decreases as the temperature decreases and abruptly goes to zero at 41 K. The films presented here are superior to those in other reports on superconducting infinite-layer thin films [10], as evidenced

(a) STEM apparatus

(b) Atomic position of $Ca_{0.96}Nd_{0.04}CuO_2$ thin film by STEM

(c) Atomic column elemental mapping by EELS

ABF: annular bright field
Nd: neodymium

Fig. 4.   Identification of superconducting state of infinite-layer $CaCuO_2$.

by the following characteristics:

- sharp superconducting transition (transition width $\Delta T_c < 1$ K)
- metal-like electronic response between 400 K and 42 K
- low resistivity value in normal state (corresponds to the intrinsic value for defect-free CuO_2 plane).

It is therefore shown that samples grown with our method are most suitable to reveal the inherent physical properties leading to understanding the mechanism of high-T_c superconductivity.

3. Infinite-layer $CaCuO_2$—elemental-resolved and atomic-resolution characterization

As already mentioned, $CaCuO_2$ is an essential structural part of high-T_c cuprates. In contrast to strontium copper oxide ($SrCuO_2$), however, little is known about the physical properties of infinite-layer $CaCuO_2$ due to the difficulty of synthesis. We synthesized infinite-layer $Ca_{1-x}Nd_xCuO_2$ thin films using MBE. In $Ca_{1-x}Nd_xCuO_2$, calcium ions (Ca^{2+} ions) are partially substituted with Nd^{3+} ions (neodymium ions) by mimicking $Sr_{0.9}La_{0.1}CuO_2$. For a composition of $x = 0.06$, we found traces of superconductivity

around 10 K [11]. It is important to note that a truly superconducting state has not been established. Therefore, it is of significant importance to determine the differences between superconducting $Sr_{1-x}La_xCuO_2$ and non-superconducting $Ca_{1-x}Nd_xCuO_2$ by using scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy (EELS).

STEM is used to visualize atomic positions in matter. The configuration of our STEM apparatus is shown in **Fig. 4(a)** [12]. Accelerated electrons at 200 kV are focused on a sample. The scattered electron beam contains information on the atomic position. This is shown in **Fig. 4(b)** for $Ca_{0.96}Nd_{0.04}CuO_2$. Because the contrast of the original bright-field image is inverted, the atomic positions appear bright in Fig. 4(b). The observed atomic column arrangements correspond to the infinite-layer structure with two-dimensional CuO_2 planes. It is evident that $Ca_{0.96}Nd_{0.04}CuO_2$ thin films are single crystalline. We used EELS to identify the constituent atomic species. This is shown in **Fig. 4(c)**. The atomic selectivity of EELS enables an atomic column identification that exactly matches the infinite-layer phase.

By measuring the distance between Cu and O

(d_{Cu-O}) from Fig. 4(c), we determined the in-plane lattice constant of $Ca_{0.96}Nd_{0.04}CuO_2$ to be 0.386 nm. This is 0.001 nm longer than for $CaCuO_2$ [13]. Similar expansion is found for the $Sr_{0.9}La_{0.1}CuO_2$ system, where a substitution of 10% of La results in an expansion of 0.002 nm of the in-plane lattice constant [14]. It is intuitively suggested that a critical in-plane lattice constant (d_{Cu-O} x 2) for the induction of superconductivity is to be expected. As the ionic size of Ca^{2+} ions is smaller than that of Sr^{2+} ions, $CaCuO_2$ has shorter d_{Cu-O} than for $SrCuO_2$. During the course of our study, we found that a higher concentration of Nd causes instability of the infinite-layer phase. Consequently, it is not possible to prepare the infinite-layer phase of $Ca_{1-x}Nd_xCuO_2$ with a sufficient amount of Nd to induce a superconducting transition. This result suggests that lattice constant (the Cu-O bond length in the CuO_2 plane) engineering is important for the induction of superconductivity in cuprates.

4. Future outlook

Infinite-layer cuprates are very important to understand the physics of high-T_c superconductivity. We plan to apply our thin film growth method to further understand the mechanism of high-T_c superconductivity commonly emerging in materials containing $CaCuO_2$. This method is currently being extended to the synthesis of superlattices containing $CaCuO_2$ [15].

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