OXYGEN CONTROL FOR EPITAXIAL GROWTH OF
CUPRATES IN ULTRAHIGH VACUUM SYSTEM

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Abstract
The oxidation ability of various oxidants for Bi$_2$Sr$_2$CaCuO$_x$ and related cuprates were evaluated both by experiments and by a thermodynamical calculation. When Bi$_2$Sr$_2$CaCu$_2$O$_x$ sputtered films were treated at 400 °C with such oxidants as photo-activated O$_2$, NO$_2$, O$_3$, and N$_2$O, significant Tc change was observed. This Tc change was found in parallel with the variation of c-lattice parameter and verified to originate from oxygen nonstoichiometry in the films by the Hall coefficient measurement. The highly oxidative property of NO$_2$, ozone, and atomic oxygen derived from this experiment was supported by the thermodynamical calculation for the oxidation of Cu$_2$O to CuO. The results were further utilized to grow alkaline earth cuprate films by pulsed laser deposition in ultrahigh vacuum (laser MBE). In situ RHEED and XPS analyses clearly indicated that alkaline earth cuprates could be grown epitaxially and laterally under such conditions as 700 °C and 1 x 10$^{-7}$ NO$_2$ pressure.

Keywords: oxygen control, superconducting film, cuprate, oxidation in UHV, laser MBE

1. INTRODUCTION
Oxygen plays a vitally important role in high Tc superconductors (HTSC), since it is a constituent of crystal lattice and is a carrier source as well. For electronic device application of HTSC, primarily required is the fabrication of HTSC thin films at low (≤ 500 °C) temperature. Optimization of oxygen content, i.e. hole concentration at low temperature is one of the key technologies and several methods were reported to be effective for this purpose. Oxygen plasma and ozone were used by Moriwaki et al.,$^1$ and Berkeley et al.,$^2$ respectively, for the oxidation of YBa$_2$Cu$_3$O$_{7-δ}$, while N$_2$O, NO$_2$, and UV light activated O$_2$ were by M. Kanai et al.,$^3$ Watanabe et al.,$^4$ and us,$^5$ respectively, for the oxidation of Bi-Sr-Ca-Cu-O system. These experimental studies were done independently and systematic comparison among the methods has scarcely been reported.

In view of the commonly observed layered perovskite structure in HTSC, we can expect to construct not only the same structure but also artificially designed new structures if a technology for atomically regulated epitaxial growth of ceramics could be established. An ultrahigh vacuum (UHV) process such as molecular beam epitaxy (MBE) should be desirable for this purpose, but it can be applied by solving the
problem of oxygen control in growing film surface in UHV.

This paper reports on fundamental problems of oxygen control at low temperature as well as in UHV condition and presents some experimental results of ceramic layer epitaxy by laser MBE which we are developing for establishing a technology of fabricating artificial ceramic lattices.

2. OXYGEN CONTROL IN Bi$_2$Sr$_2$CaCu$_2$O$_x$ FILMS BY ACTIVATED OXYGENs

The oxygen control in a superconducting thin films and the verification of its effect on Tc were investigated by exposing sputter-deposited Bi$_2$Sr$_2$CaCu$_2$O$_x$ (Tc, onset = 80K) films to several active oxygen compounds at 400°C. Relationships were evaluated among Tc, c-lattice parameter, and Hall coefficient of the oxygen treated films and discussed in relation to the oxygen nonstoichiometry.

2-1. EXPERIMENTAL

An ac sputtering apparatus shown in Fig.1 was used for both film synthesis and oxygen treatment. A pair of disc Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ targets mounted on the glass-covered copper rods were sputtered by the application of 50 Hz ac high voltage to deposit thin films of about 0.8μm in 2h on yttria stabilized zirconia (YSZ) substrates. As-deposited films were annealed at 850°C for 30 min to show XRD patterns almost identical to that of c-axis oriented Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ phase. The film specimens thus prepared have Tc onset of about 80K. Oxygen, ozone and nitrous oxide with or without UV light irradiation and oxygen plasma were employed for oxygen treatments. The oxygen plasma was generated at 0.4 Torr of O$_2$ by the application of ac 3.6 kV between a pair of stainless-steel electrodes, which were replaced from the targets after the film deposition, facing each other 6 cm apart. Ozone was generated by using a micro ozonizer (Erstat Laboratory AOC-05) and introduced in the apparatus. Every activated oxygen treatment of the film was carried out at 400°C for 30 min and at decreasing temperatures to about 50°C for additional 30 min.

The resistivity of the films was measured by the dc four probe method. The crystal structure of the films was analyzed using an X-ray diffractometer (XRD, Mac Science MXP-3, CuKα). Hall coefficient of the films was measured by standard van der Pauw technique at room temperature under a magnetic field of 1 T.

2-2. RESULTS and DISCUSSION

Figure 2 shows the temperature dependence of resistivity for some of the specimens after activated oxygen treatments. The application of ozone (C) or oxygen plasma (D) decreased the Tc onset of the film from 80K to about 60K. Activated oxygen treatments did not produce a new XRD peak but gave small shifts towards higher diffraction angles in the c lattice constants. The Tc values of these films returned to about 80K when the films were subjected to further heat treatment in atmospheric oxygen without the light irradiation. All these results were essentially
the same as in the case of UV light irradiation in the presence of atmospheric oxygen and prompted us to consider that these activated oxygen treatments should increase the oxygen content in the films and induce the decrease of c lattice constant and critical temperature.

On the other hand, the treatment of film with 400 Torr N2O under UV light irradiation increased the Tc onset from 80K to 100K (Fig.2, (E)). The XRD (00c) peaks shifted towards lower diffraction angles. This film gave the Tc onset of about 60K and higher diffraction angles after the treatment of atmospheric oxygen with the UV light irradiation. These Tc changes were reversible, which means the Tc changes were induced only by the change of oxygen content in the film. Oxygen treatments activated by UV light and plasma worked to incorporate the oxygen into the films, whereas N2O treatment with UV light irradiation apparently worked to reduce the oxygen content in the film. This effect of N2O/UV treatment was rather contrary to our intuition, since atomic oxygen should also be formed from N2O by the UV light irradiation. The adsorption of N2O and oxygen extraction from the oxide film surface to liberate N2 and O2 can be the origin of reducing effect of N2O.

The Tc onset of the oxygen treated films could be linearly correlated with the c-lattice length up to 3.072 nm. However, films with c-parameter longer than 3.075 nm became semiconductive. Kinetics should also be taken into account for the oxygen control in the film, since the activated oxygen treatment at room temperature gave almost no change in Tc.

Hall coefficients (RH) were measured for the specimens treated under three typical activated oxygen treatments listed in Tab. 1. The signs of the RH were positive, suggesting that the charge carrier was hole. Table 1 also shows the relationship between the hole concentration (1/eRH) and Tc. The hole concentration is consistent with the oxidation behavior described above; the overdoping of hole carriers in Bi2Sr2CaCu2Ox film by highly active oxidants induced the Tc decrease.

3. THERMODYNAMICAL CONSIDERATION ON OXIDATION ABILITY OF OXIDANTS

From the above study, the high oxidation ability of NO2, photochemically activated O2, and ozone were qualitatively confirmed. Then we tried to evaluate the

![Fig.2. Temperature dependence of resistivity for Bi2Sr2CaCu2Ox films treated by some activated oxygens. (A) O2 1 atm, (B) O2 1 atm/UV, (C) O2 1 atm, (D) Oxygen plasma, (E) N2O 400 Torr/UV.](image)

<table>
<thead>
<tr>
<th>specimen</th>
<th>activated oxygen treatment condition</th>
<th>Tc onset (K)</th>
<th>RH (10^-3 cm^3/C)</th>
<th>NH (1/eRH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>O2 1 atm / UV</td>
<td>69</td>
<td>4.0</td>
<td>1.6</td>
</tr>
<tr>
<td>G</td>
<td>O2 1 atm</td>
<td>91</td>
<td>6.0</td>
<td>1.0</td>
</tr>
<tr>
<td>H</td>
<td>N2O 400 Torr / UV</td>
<td>103</td>
<td>7.2</td>
<td>0.87</td>
</tr>
</tbody>
</table>
oxidation ability of various oxidants quantitatively by thermodynamical calculation so that we could estimate the possibility of as-grown oxide film growth even in UHV condition. In the calculation, the coexistence of Cu2O/CuO in the following seven equilibria was assumed:

\[
\begin{align*}
2\text{Cu}_2\text{O}(s) + 2\text{O}_2(g) & \rightleftharpoons 4\text{CuO}(s) \quad (1) \\
3\text{Cu}_2\text{O}(s) + \text{O}_3(g) & \rightleftharpoons 6\text{CuO}(s) \quad (2) \\
\text{Cu}_2\text{O}(s) + 2\text{O}_2(g) & \rightleftharpoons 2\text{CuO}(s) \quad (3) \\
\text{Cu}_2\text{O}(s) + 3\text{O}_2(g) & \rightleftharpoons 2\text{CuO}(s) + \text{O}_2(g) \quad (4) \\
\text{Cu}_2\text{O}(s) + \text{N}_2\text{O}_2(g) & \rightleftharpoons 2\text{CuO}(s) + \text{N}_2(g) \quad (5) \\
4\text{Cu}_2\text{O}(s) + 2\text{N}_2\text{O}_2(g) & \rightleftharpoons 8\text{CuO}(s) + 2\text{N}_2(g) \quad (6) \\
2\text{Cu}_2\text{O}(s) + 2\text{N}_2\text{O}(g) & \rightleftharpoons 2\text{CuO}(s) + 2\text{N}_2(g) \quad (7) \\
\end{align*}
\]

In the equilibria (1) through (3), variation of Gibbs free energy (\(\Delta G\)) obeys the following formula by assuming that the activity of solids is equal to unity:

\[\Delta G = \Delta G^0 - RT \ln P_{\text{ox}}\]

In the system including two gas components (reactions (4)-(7)), the relationship between the gas pressure and temperature cannot be uniquely determined because the number of degree of freedom is 2 by the phase rule. The variation of Gibbs free energy (\(\Delta G\)) for reaction (4) obeys the following formula. Here, the activity of solids is again unity:

\[\Delta G = \Delta G^0 + RT \ln \left(\frac{P_{\text{O}_2}}{P_{\text{O}_3}}\right)\]

In the equilibrium, \(\Delta G\) is zero. Further, we can assume the total pressure to be below \(10^{-8}\) bar in the MBE conditions. Therefore, when Cu2O and CuO coexist, \(\log P_{\text{O}_3}\) is approximated by the next formula:

\[\log P_{\text{O}_3} = \log(\exp(\Delta G^0/RT)) + (1/\log e)(10^{-8})\]

From the Gibbs free energy of formation listed in the JANAF Thermodynamic Table, variations of Gibbs free energy (\(\Delta G^0(T, 1\ \text{bar})\)) of the reactions (1)-(7) were calculated at 300 K, 400 K, 500 K, 700 K, and 1000 K.

Figure 3 shows the relationship between the oxidant gas pressure and temperature for coexistence conditions of Cu2O and CuO. An almost linear relationship was obtained between the logarithm of oxidant gas pressure and reciprocal of temperature. CuO is stable above the line. Ozone and atomic oxygen have oxidation abilities stronger than \(\text{O}_2\). Also \(\text{N}_2\text{O}\) and \(\text{NO}_2\), which are not explosive and can be easily obtained with high purity, proved to have an oxidation ability even in UHV condition.

4. ATOMIC LAYER EPITAXY OF ALKALINE EARTH CUPRATES FILMS BY LASER MBE

All the known high Tc (\(\geq 40\) K) superconductors have layered perovskite structure containing CuO2 slab. Therefore, we can expect not only to reproduce the structure but also to construct artificially modified new structures, which can exhibit still higher Tc superconductivity, by establishing the processing technology of ceramic layer epitaxy, defined as the epitaxial layer-by-layer growth of ceramic thin films. For this purpose it is essential to diagnose the crystal structure and optimize the oxygen content in the growing film by monitoring the surface with reflection high energy electron diffraction (RHEED), as it is proven...
in the fabrication of semiconductor superlattices.

Since RHEED is usually operated in UHV, we must overcome the problem of oxidation in UHV to apply in situ RHEED for the growth of oxide films. From the studies described above, it was considered possible to deposit oxide films with appropriate oxygen contents even in UHV conditions.

4-1. EXPERIMENTAL

Figure 4 illustrates the laser MBE system we used for the ceramic layer epitaxy. The system is equipped with in situ RHEED and XPS. A focused pulsed ArF excimer laser beam (duration of 20ns, frequency of 2 - 10 Hz, and pulse energy of 80 mJ/shot) was impinged with an energy density of 1 J/cm² through a quartz window onto a sintered (AE)CuO₂ (AE=Ca, Sr, or their mixtures) target to deposit a film on SrTiO₃ (001) substrates heated at 550 °C - 700 °C. NO₂ was flushed onto the substrate at a pressure between 1 x 10⁻⁷ and 1 x 10⁻³ Torr.

Film thickness was measured by the stylus method. Typical deposition rate was 0.3 nm/min in case of 2 Hz pulsed laser repetition. The structure of films was characterized by X-ray diffractometer (XRD) with monochromated Cu Kα radiation. The electrical resistivity was measured by the standard four probe method in the temperature range between 7 K and 300 K.

4-2. RESULTS AND DISCUSSION

(1) Structure of (Sr₁₋ₓCaₓ)CuO₂₋ᵧ films

Conditions and results of (Sr₁₋ₓCaₓ)CuO₂₋ᵧ film growth are summarized in Table 2. From the XRD analysis of deposited films, SrCuO₂₋ᵧ

Table 2. Results on the preparation of (Sr₁₋ₓCaₓ)CuO₂₋ᵧ films (x = 0, 0.5, 0.86 and 1) by laser MBE.

<table>
<thead>
<tr>
<th>Target composition (Sr:Ca):Cu</th>
<th>NO₂ pressure (x10⁻⁷Torr)</th>
<th>Substrate temp. (ºC)</th>
<th>XPS Iₓ/Iₓ⁺⁺</th>
<th>RHEED pattern</th>
<th>XRD c-axis length (nm)</th>
<th>(Sr, Ca)CuO₂ rocking curve FWHM of (002) (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0:1</td>
<td>750</td>
<td>0.14</td>
<td>spot c)</td>
<td>0.347</td>
<td>0.47</td>
<td>c)</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.38</td>
<td>streak</td>
<td>0.345</td>
<td>0.32</td>
<td>d)</td>
</tr>
<tr>
<td>5</td>
<td>775</td>
<td>0.54</td>
<td>ring d)</td>
<td>not measured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>750</td>
<td>0.19</td>
<td>spot</td>
<td>unknown peaks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5:0.5:1</td>
<td>700</td>
<td>0.24</td>
<td>streak</td>
<td>0.332</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.32</td>
<td></td>
<td>0.332</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>0.14:0.86:1</td>
<td>700</td>
<td>0.40</td>
<td>spot</td>
<td>0.325</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>0:1:1</td>
<td>700</td>
<td>not measured</td>
<td>spot</td>
<td>(101) // sub. oriented</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aXPS peak area ratio of the satellite to the main for Cu 2p 1/2.
*bStreaky RHEED patterns indicated the film orientation of (Sr,Ca,_)CuO₂ - (001)//SrTiO₃(001) and (Sr,Ca,_)CuO₂ //SrTiO₃[010].
*²Mixed phases of Sr₂CuO₄ and SrCu₂O₄.
*³Mixed phases of Sr₂CuO₄ and orthorhombic-SrCuO₂.
*⁴Only one peak observed at d=0.243nm is assigned to CaCuO₂ 101 (d=0.244nm).
and (Sr0.5Ca0.5)CuO2-y films were confirmed to be grown epitaxially in the tetragonal phase, when (1 - 5) x 10^{-7} Torr NO2 was present in the chamber. The oxidation states of copper in the as-grown (Sr1-xCax)CuO2-y (x = 0, 0.5, 0.86) films were essentially the same (Cu^{2+}) as in CuO judging from their XPS satellite structures in Cu 2p core level spectra as well as from the kinetic energy of Cu L3M45M45 Auger peak. Therefore, y should be close to zero.

Figure 5 shows the phase diagram for Sr-Cu-O system as functions of NO2 pressure and substrate temperature. The optimum conditions for the growth of tetragonal SrCuO2-y films were at about 700°C and NO2 pressure of 1 x 10^{-7} Torr. In the absence of NO2, films were in mixed phases and contained Cu in both mono- and di-valent states, as verified by XRD and XPS, respectively.

(2) Growth mode of (Sr1-xCox)CuO2-y films

RHEED patterns for the (Sr0.5Ca0.5)CuO2-y and SrCuO2-y film growth at 700°C and 1x10^{-7} Torr NO2 varied with the deposition time. As soon as the film deposition started, the RHEED pattern changed from the substrate streaks into broad spots. After 1 to 2 nm thick film growth, the RHEED pattern returned to be streaks. Figure 6 (b) shows the intensity oscillation observed at the RHEED central streak during the SrCuO2-y film deposition. The oscillation period of 0.33 nm is the same as the (001) interplane distance of tetragonal SrCuO2, indicating that the film was grown by a layer-by-layer mode, i.e. by stacking two-dimensional SrCuO2-y unit cells. Figure 6 also shows a significant effect of NO2 gas pressure on the layer-by-layer growth. The RHEED intensity oscillation was observed clearly under the condition optimum for the epitaxial growth of tetragonal SrCuO2-y.

(3) Electric property

As-grown SrCuO2-y and (Sr0.5Ca0.5)CuO2-y films in tetragonal phase had black color and very low resistivities in the order of 10^{-3} S^{-1}cm. On the other hand,

![Fig. 5. Phase diagram of Sr-Cu-O system prepared by laser MBE under the various substrate temperatures and NO2 gas pressures.](image)

![Fig. 6. RHEED intensity oscillations during the deposition of SrCuO2-y films at 700°C under various NO2 pressures.](image)
mixed phase films prepared in the absence of NO2 were insulative. The tetragonal phase films had resistivities decreasing linearly with the temperature decrease from 300 K to 7 K. Such a metallic behavior of SrCuO2-y film was observed for the first time and attracts our interest in the development of superconductivity by a slight modification of composition, lattice structure, and/or oxygen nonstoichiometry.

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