OXYGEN CONTROL FOR EPITAXIAL GROWTH OF CUPRATES IN ULTRAHIGH VACUUM SYSTEM

超高真空系における酸化物高温超伝導体の酸素制御

Hideomi Koinuma

Research Laboratory of Engineering Materials

Tokyo Institute of Technology

4259 Nagatsuta, Midori-ku, Yokohama 227

Tel. 81-45-922-1111 Fax. 81-45-921-1015

(Received 17, December 1991 Accepted 18, December 1991)

Abstract

The oxidation ability of various oxidants for $\text{Bi}_2\text{Sr}_2\text{CaCuO}_x$ and related cuprates were evaluated both by experiments and by a thermodynamical calculation. When $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ sputtered films were treated at 400°C with such oxidants as photo-activated O_2 , NO_2 , O_3 , and N_2O , significant T_c change was observed. This T_c 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_2O 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 1×10^{-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 T_c 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 ($\leq 500^\circ\text{C}$) 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 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, while N_2O , 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 $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ FILMS BY ACTIVATED OXYGENS

The oxygen control in a superconducting thin films and the verification of its effect on T_c were investigated by exposing sputter-deposited $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (T_c , onset = 80K) films to several active oxygen compounds at 400°C. Relationships were evaluated among T_c , 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.⁶ A pair of disc $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ targets mounted on the glass-covered copper rods were sputtered by the

Fig.1. The schematic representation of the ac 50 Hz sputtering apparatus.

application of 50 Hz ac high voltage to deposit thin films of about 0.8 μm 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 $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ phase. The film specimens thus prepared have T_c 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, $\text{CuK}\alpha$). 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 T_c 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 T_c 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 (B)⁵ 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 T_c onset from 80K to 100K (Fig.2, (E)). The XRD (00c) peaks shifted towards lower diffraction angles. This film gave the T_c onset of about 60K and higher diffraction angles after the treatment of atmospheric oxygen with the UV light irradiation. These T_c changes were reversible, which means the T_c 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 T_c 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 T_c.

Hall coefficients (R_H) were measured for the specimens treated under three typical activated oxygen treatments listed in Tab. 1. The signs of the R_H were positive, suggesting that the charge carrier was hole. Table 1 also shows the relationship between the hole concentration (1/eR_H) and T_c. The hole concentration is consistent with the oxidation behavior described above; the overdoping of hole carriers in Bi₂Sr₂CaCu₂O_x film by highly active oxidants induced the T_c decrease.

Fig.2. Temperature dependence of resistivity for Bi₂Sr₂Ca₁Cu₂O_x films treated by some activated oxygens. (A) O₂ 1 atm, (B) O₂ 1 atm/UV, (C) O₃ 1 atm, (D) Oxygen plasma, (E) N₂O 400 Torr/UV.

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

Table 1. Activated oxygen treatment conditions, T_c onset, Hall coefficients and carrier concentrations.

specimen	activated oxygen treatment condition	T _c ^{onset} (K)	R _H (10 ⁻³ cm ³ /C)	N _H (=1/eR _H) (10 ²¹ cm ⁻³)
F	O ₂ 1 atm / UV	69	4.0	1.6
G	O ₂ 1 atm	91	6.0	1.0
H	N ₂ O 4 Torr / UV	103	7.2	0.87

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.⁷

In the calculation, the coexistence of $\text{Cu}_2\text{O}/\text{CuO}$ in the following seven equilibria was assumed:

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

$$\Delta G = \Delta G^\circ_{\text{ox}} - RT \ln p_{\text{ox}}$$

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 (ΔG) for reaction (4) obeys the following formula. Here, the activity of solids is again unity:

$$\Delta G = \Delta G^\circ + RT \ln (p_{\text{O}_2}/p_{\text{O}_3})$$

In the equilibrium, ΔG is zero. Further, we can assume the total pressure to be below 10^{-8} bar in the MBE conditions. Therefore, when Cu_2O and CuO coexist, $\log p_{\text{O}_3}$ is approximated by the next formula:

$$\log p_{\text{O}_3} = \log(\exp(\Delta G^\circ/RT)) + (1/\log_e 10) \cdot \ln 10^{-8}$$

From the Gibbs free energy of formation listed in the JANAF Thermodynamic Table, variations of Gibbs free energy ($\Delta G^\circ(T, 1 \text{ bar})$) 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 Cu_2O 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 O_2 . Also N_2O and 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 T_c (≥ 40 K) superconductors have layered perovskite structure containing CuO_2 slab. Therefore, we can expect not only to reproduce the structure but also to construct artificially modified new structures, which can exhibit still higher T_c superconductivity, by establishing the processing technology of ceramic layer epitaxy, defined as the epitaxial layer-by-layer growth of ceramic thin films.⁸ 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

Fig. 3. Calculated coexistence lines of Cu_2O and CuO for the reactions (1) through (7) in the text. Pox. gas in bar.

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

Fig.4. Schematic diagram of laser MBE apparatus with in situ RHEED and in situ XPS analyzers.

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 10⁻⁵ 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 K α 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 (Sr_{1-x}Ca_x)CuO_{2-y} (0 ≤ x ≤ 1) films

Conditions and results of (Sr_{1-x}Ca_x)CuO_{2-y} film growth are summarized in Table 2. From the XRD analysis of deposited films, SrCuO_{2-y}

Table 2. Results on the preparation of (Sr_{1-x}Ca_x)CuO_{2-y} films (x = 0, 0.5, 0.86 and 1) by laser MBE.

Target composition (Sr:Ca):Cu	NO ₂ pressure (x10 ⁻⁷ Torr)	Substrate temp. (°C)	XPS I _s /I _m ^(a) Cu2p1/2	RHEED ^(b) pattern	XRD; c-axis length (nm)	(Sr,Ca)CuO ₂ rocking curve FWHM of (002) (deg.)
1 : 0 : 1	1	750	0.14	spot	c)	c)
		700	0.38	streak	0.347	0.47
	5	775	not measured	ring	0.345	0.32
0.5 : 0.5 : 1	0.1		0.19	spot	unknown peaks	
	1	700	0.24	streak	0.332	0.43
			0.32		0.332	0.39
0.14 : 0.86 : 1	1	700	0.40	spot	0.325	0.85
0 : 1 : 1	1	700	not measured	spot	(101)//sub. oriented ^(c)	

^{a)}XPS peak area ratio of the satellite to the main for Cu 2p 1/2.

^{b)}Streaky RHEED patterns indicated the film orientation of (Sr_xCa_{1-x})CuO_y - (001)//SrTiO₃(001) and (Sr_xCa_{1-x})CuO_y[010]//SrTiO₃[010].

^{c)}Mixed phases of Sr₂Cu^{II}O₃ and SrCu^I₂O₂.

^{d)}Mixed phases of Sr₂CuO₃ and orthorhombic-SrCuO₂.

^{e)}Only one peak observed at d=0.243nm is assigned to CaCuO₂ 101 (d=0.244nm).

and $(\text{Sr}_{0.5}\text{Ca}_{0.5})\text{CuO}_{2-y}$ films were confirmed to be grown epitaxially in the tetragonal phase, when $(1 - 5) \times 10^{-7}$ Torr NO_2 was present in the chamber. The oxidation states of copper in the as-grown $(\text{Sr}_{1-x}\text{Ca}_x)\text{CuO}_{2-y}$ ($x = 0, 0.5, 0.86$) 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 $\text{L}_{3\text{M}_{45}\text{M}_{45}}$ Auger peak.⁹ Therefore, y should be close to zero.

Figure 5 shows the phase diagram for Sr-Cu-O system as functions of NO_2 pressure and substrate temperature. The optimum conditions for the growth of tetragonal SrCuO_{2-y} films were at about 700°C and NO_2 pressure of 1×10^{-7} Torr. In the absence of NO_2 , 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 $(\text{Sr}_{1-x}\text{Ca}_x)\text{CuO}_{2-y}$ films

RHEED patterns for the $(\text{Sr}_{0.5}\text{Ca}_{0.5})\text{CuO}_{2-y}$ and SrCuO_{2-y} film growth at 700°C and 1×10^{-7} Torr NO_2 varied with the deposition time.

Fig. 5. Phase diagram of Sr-Cu-O system prepared by laser MBE under the various substrate temperatures and NO_2 gas pressures.

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 SrCuO_{2-y} film deposition. The oscillation period of 0.33 nm is the same as the (001) interplane distance of tetragonal SrCuO_2 , indicating that the film was grown by a layer-by-layer mode, i. e. by stacking two-dimensional SrCuO_{2-y} unit cells.¹⁰ Figure 6 also shows a significant effect of NO_2 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 SrCuO_{2-y} .

(3) Electric property

As-grown SrCuO_{2-y} and $(\text{Sr}_{0.5}\text{Ca}_{0.5})\text{CuO}_{2-y}$ films in tetragonal phase had black color and very low resistivities in the order of $10^{-3} \text{ S}^{-1}\text{cm}$. On the other hand,

Fig. 6. RHEED intensity oscillations during the deposition of SrCuO_{2-y} films at 700°C under various NO_2 pressures.

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 SrCuO_{2-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.

ACKNOWLEDGEMENTS

The author expresses his sincere thanks to Drs. M. Yoshimoto and T. Hashimoto and Messers H. Nagata, T. Tsukahara, and S. Gonda for their collaboration. This work was supported in part by the grant-in-aid for Scientific Research on Chemistry of New High T_c Superconductors from Ministry of Education, Science and Culture of Japan.

REFERENCES

- ¹K. Moriwaki, Y. Enomoto, S. Kubo, T. Murakami, Jpn. J. Appl. Phys., 27, L2075(1988)
- ²D. D. Berkeley et al., Appl. Phys. Lett., 53, 1973(1988)
- ³M. Kanai, T. Kawai, S. Kawai, H. Tabata, Appl. Phys. Lett., 54, 1802(1989)
- ⁴S. Watanabe, M. Kawai, T. Hanada, Jpn. J. Appl. Phys., 29, L1111 (1990)
- ⁵K. Takeuchi, M. Kawasaki, M. Yoshimoto, Y. Saito, H. Koinuma, Jpn. J. Appl. Phys., 29, L70(1990)
- ⁶S. Nagata, M. Kawasaki, H. Koinuma, Jpn. J. Appl. Phys., 27, L870(1988)
- ⁷T. Hashimoto, H. Koinuma, K. Kishio, Jpn. J. Appl. Phys., 30, 1685(1991)
- ⁸H. Koinuma, H. Nagata, T. Tsukahara, S. Gonda, M. Yoshimoto, Appl. Phys. Lett., 58, 2027(1991)
- ⁹A. Fujimori, E. T. Muromachi, Y. Uchida, B. Okai, Phys. Rev. B, 35, 8814(1987)
- ¹⁰T. Tsukahara, M. Yoshimoto, H. Nagata, T. Hashimoto, S. Gonda, H. Koinuma, Solid State Ionics, in press

***The 2nd Tokai University
International Workshop
on
SUPERCONDUCTIVITY
(TUIWS)***

October 9-12, 1991

**Tokai University Pacific Center
2241 Kapiolani Blvd. Honolulu, Hawaii
(Phone: 808-973-4100 Fax: 808-973-4107)**

CONFERENCE ORGANIZERS

Organizing Committee (Tokai University)

Chair; Tatsuro MATSUMAE
(President of Tokai University)
Sonosuke KATORI
Shoji YOSHIDA
Kimikazu MATSUYAMA
Norio MATSUMAE
Yoshio MIHARA
Hajime YANO
Takashi MATSUMOTO
Toru HIRAYAMA
Mamoru KAWAKAMI

Conference Organizers

Chair; Sadao NAKAJIMA
Co-Chair; Shoji TANAKA
Co-Chair; Kyoji TACHIKAWA
Mamoru KAWAKAMI
Hideomi KOINUMA

Program Committee

Chair; Tadashi SHIRAISHI
Hideomi KOINUMA
Kazumasa TOGANO
Naoto NAGAOSA
Yoshitake NISHI
Yuh SHIOHARA

Secretariat

Chair; Tadashi SHIRAISHI
Ichiro NAKADA
Shusuke YOMO
Yasunari KURIHARA
Tetsunobu TAKAYAMA
Minoru HAYAMA
Masaaki IGARASHI