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PREPARATION AND CHARACTERISTICS OF SUPERCONDUCTING CUPRATE THIN FILMS: $Nd_{2-x}Ce_xCuO_4$ AND SUBSTITUTED Bi-SYSTEM

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ABSTRACT Characteristics of the electron-doped-type $Nd_{2-x}Ce_xCuO_4$ system and substituted Bi-system have been studied using the high quality thin-film samples grown by rf-magnetron sputtering and/or subsequent heat-treatment. The $Nd_{2-x}Ce_xCuO_4$ samples with excellent superconducting properties were obtained in thin films and their optical and X-ray photoelectron spectroscopy (XPS) studies were performed in regard to the Ce content and reducing treatment. Substituted Bi-Sr-Ln-Cu-O thin films have also been prepared and growth conditions for Bi-system with 2-2-1-2 and 2-2-2-2 phases were found. Moreover, new 2-2-1-2 phase in the simple Bi-Sr-Cu-O system was fabricated by thin-film processing and 80-K superconductivity was obtained.

1. INTRODUCTION

A great deal of interests have been focused to the thin films processing of high-Tc superconductors for not only the viewpoint of device applications but the scientific research. Thin-film processing has an ability to create a metastable phase which cannot be made by solid state reaction technics, i.e. ceramics method. For instance, 1-2-4 phase ($YBa_2Cu_4O_y$) or 2-2-3-4 phase ($Bi_2Sr_2Ca_3Cu_4O_y$) was firstly prepared in the thin film samples [1,2]. In addition to the fabrication of new phases, thin film processing enable the preparation of superconducting samples with excellent quality. High Jc (critical current density) samples were realized in the single-crystalline thin films epitaxially grown on adequate single crystal substrates [3]. For electron-doped $(Nd,Ce)_2CuO_4$ system, excellent superconducting properties were easily obtained in thin films rather than in bulk ceramic samples, which may be responsible for the facility of reducing treatment in the films [4]. Thus, in some cases, thin films and thin-film processing are very useful for the research on the nature of high-Tc superconductors.

In this paper, we describe the thin films of two systems; one is electron-doped $(Nd,Ce)_2CuO_4$ system with a variety of Ce content and the other is the lanthanoid (Ln) substituted bismuth-system, Bi-Sr-Ln-Cu-O. Their preparation methods, electric properties, x-ray photoemission were studied.

2. FILM PREPARATION

Thin films were prepared by the rf-planar magnetron sputtering and subsequent annealing. Targets were complex oxides of constituents, which were made by calcining the adequate mixture of each oxides. The diameter of the target was 100 mm. Substrates used were (100) plane of MgO or (100) plane of $SrTiO_3$ single crystals and heated at 400-700°C during deposition. Sputtering was carried out in the argon and oxygen mixed atmosphere with an input power of about 150 W and gas pressure of 0.5 Pa. The appeared phases in the films were controlled during the deposition or the post-annealing procedures.

One of the compounds we intended to prepare is $(Nd,Ce)_2CuO_4$ system which was found to be the "n-type" material with electrons as the charge carriers [5]. Since excellent superconductivity is easily obtained in film samples of this system, $(Nd,Ce)_2CuO_4$ thin films are suitable for a basic research. The other compounds are Bi-based materials with lanthanoid substitution, Bi-Sr-Ln-Cu-O. The interesting viewpoint is the feasibility of "n-type" in the Bi-system. From the similar consideration to the $(Nd,Ce)_2CuO_4$ system, we dealt with Bi-Sr-(Nd,Ce)-Cu-O thin films. Appearance of crystal phases in thin films of this system was studied. Moreover in the course of the experiments, construction of metastable structure in Bi-based thin films with no lanthanoid elements, i.e. simple Bi-Sr-Cu-O system, was investigated.

3. $(Nd,Ce)_2CuO_4$ THIN FILMS

3.1 SUPERCONDUCTING PROPERTIES

The $Nd_{2-x}Ce_xCuO_4$ thin films with various Ce content, x, have been prepared. (100) plane of perovskite $SrTiO_3$ were selected as a substrate and heated at around 500°C during deposition. The crystallinity of the as-deposited films showed the polycrystalline structure of the T' phase (Nd_2CuO_4 structure) with weakly preferred c-axis orientation. In order to improve crystallinity, the films were post-annealed at 1100°C for 2 hours in air, followed by quenching. The films showed a highly oriented structure with the c-axis normal to the substrate after the annealing, as shown in Fig.1 for the x=0.15 film. As x increased from 0 to 0.18, the c-axis lattice constant decreased from 1.215 nm to 1.203 nm. The electric properties of the films showed semiconductor-like behavior. Superconductivity was induced by the subsequent reducing treatment. This treatment was done by annealing the films in a vacuum (10^{-1} -10^{-4} Pa).

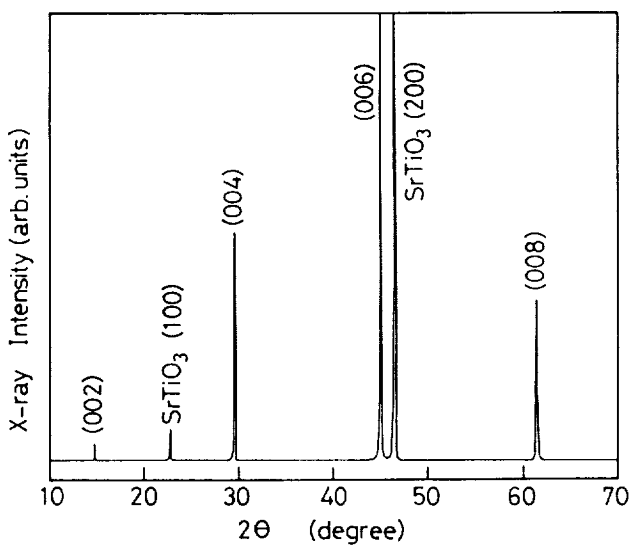

Fig.1. X-ray diffraction pattern of the $Nd_{1.85}Ce_{0.15}CuO_4$ film.

Figure 2 shows the temperature dependence of the resistivity for the films with various Ce content x ($0 \leq x \leq 0.23$) after reduction. Metallic behavior was observed for $x \geq 0.10$. Superconductivity was observed for $0.14 \leq x \leq 0.18$. With increasing x from 0.14 to 0.18, Tc tended to lower, similarly to bulk samples [6]. The Hall coefficient R_H was negative in the normal state, indicating that the charge carriers are electrons.

The diamagnetism (shielding effect) of the films were measured by an rf SQUID magnetometer under a magnetic field of 10 Oe. Figure 3 shows the temperature dependence of the diamagnetization for the films with various x after the reduction. For the x=0.15 film, the diamagnetization rapidly decreased at around 20 K with increasing the temperature and was observed up to 25 K. According to Bean's formula, the diamagnetization at 4.2 K for the

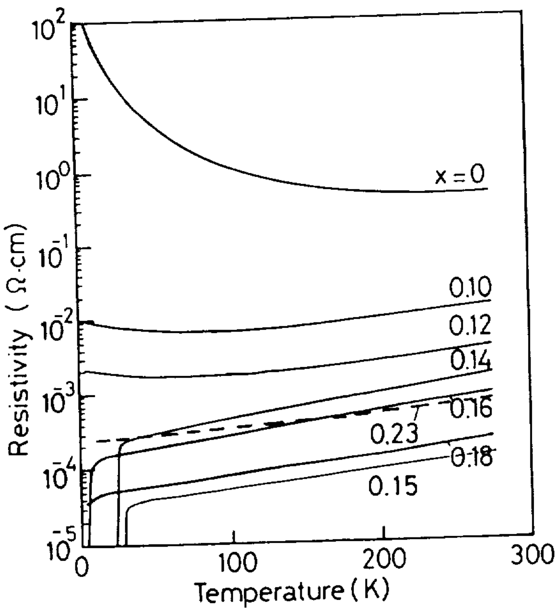

Fig.2. Temperature dependence of the resistivity for $Nd_{2-x}Ce_xCuO_4$ films after reduction.

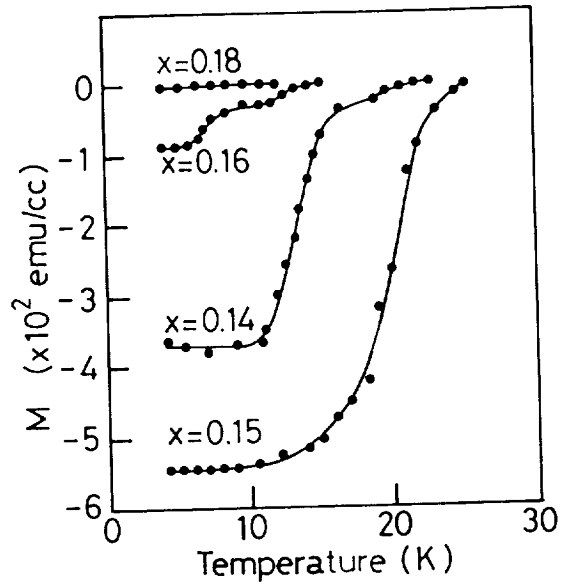

Fig.3. Temperature dependence of the diamagnetization for $Nd_{2-x}Ce_xCuO_4$ films.

x=0.15 film corresponds to a critical current density of 7×10^5 A/cm^2, which is consistent with the result of electrical measurement. The diamagnetization is highly dependent on x. The value at 4.2 K remarkably decreased as x deviates from 0.15.

3.2 OPTICAL PROPERTIES

To investigate the change of the electronic state by the Ce doping, optical properties such as reflectivity and absorption spectra were measured from 0.4 to 2.5 µm [7]. The polarization of the incident light was normal to the c-axis. There was no appreciable change in spectra before and after reduction except for the x=0 film.

Figure 4 shows the reflectivity spectra. For the Nd_2CuO_4 film (x=0), some features were observed, but no sign of plasma reflection. With increasing the Ce content x up to 0.12, a Drude-like plasma reflection appeared. At higher x of $0.14 \leq x \leq 0.16$, the reflection became much clearer with a plasma edge at around 1.0 µm. The solid lines in this figure are the Drude fits. The plasma frequency w_p was estimated to be 1.1 eV, and was almost constant over the range of $0.14 \leq x \leq 0.18$. The w_p value is about 0.2 eV larger than that of $(La,Sr)_2CuO_4$ system [8], but its constant behavior against dopant concentration is common.

Figure 5 shows the absorption spectra. A solid line for x=0 shows the absorption spectrum of the Nd_2CuO_4 film before reduction. The intense absorption below 1 µm seems to originate from the interband transition with an energy gap of 1.3eV. According to the Mott-Hubbard energy scheme, it may be interpreted as a charge transfer excitation between the O 2p states (valence band) and the upper Hubbard band (conduction band). Suzuki [8] reported an

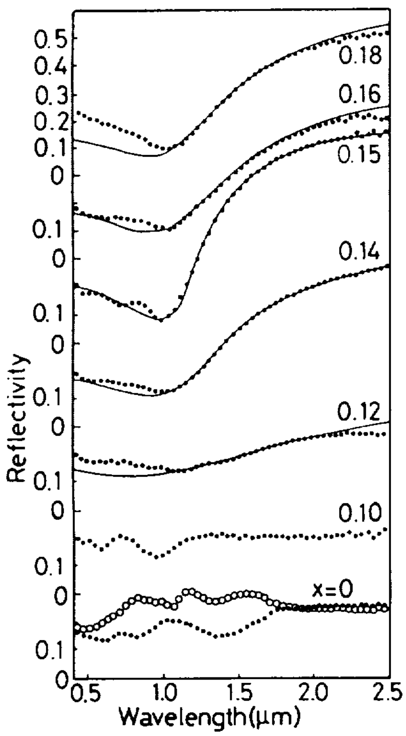

Fig.4. Optical reflectivity spectra for the $Nd_{2-x}Ce_xCuO_4$ thin films.

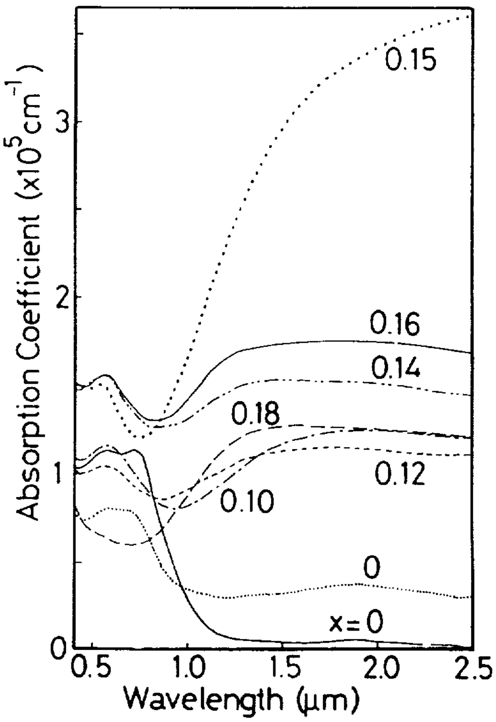

Fig.5. Optical absorption spectra for the $Nd_{2-x}Ce_xCuO_4$ thin films.

energy gap of 2.0 eV for La_2CuO_4 single crystal film, and Tajima et al. [9] observed charge transfer excitation at 2.0 and 1.5 eV for La_2CuO_4 and Nd_2CuO_4 single crystals, respectively. These gap energies may be inherent in different Cu-O configurations, octahedra for La_2CuO_4 and squares with no apical oxygen for Nd_2CuO_4.

As x increases from 0 to 0.12, the interband absorption decreased and a broad absorption appeared in the near-infrared region. In the superconducting compositional region, $0.14 \leq x \leq 0.18$, the spectra were dominated by the near-infrared absorption and the interband absorption was completely suppressed at x=0.18.

These features reflect the change of the electronic state by the electron doping into the conduction band, which evolves from the semiconducting state to the metallic state. The integrated oscillator strength in this spectral region was enhanced in the superconducting compositional region. This may suggest the development of density states and its correlation with Tc.

3.3 X-RAY PHOTOEMISSION STUDY

X-ray photoemission spectra were measured with a hemispherical electron spectrometer in a vacuum pressure less than 3×10^{-8}Pa. The measurement of the spectra was carried out after in-situ scrape of the film surface with a diamond file until no further change in the photoemission spectra was observed. The Cu $2p_{3/2}$ electron spectra for the $Nd_{2-x}Ce_xCuO_4$ films where x is 0, 0.15 and 0.23 were collected after the reducing treatment. Figure 6 (a), (b), and (c) shows the results for x=0, 0.15, and 0.23 thin films, respectively. From the observed binding energies and line widths of peaks, it was revealed that electron doping from the semiconducting Nd_2CuO_4 (x=0), where Cu valence is +2, gave rise to Cu^{1+} ion formation [10]. The valence for Cu of the $Nd_{1.85}Ce_{0.15}CuO_4$ superconducting film is +1. However, further doping of Ce seemed to result in the recreation of Cu^{2+} as shown in the x=0.23 film because the satellite peak is observed.

Then, the effect of reducing treatment was studied by the XPS using $Nd_{1.85}Ce_{0.15}CuO_4$ thin films of before and after the reduction. Before the reducing treatment, there existed Cu^{2+} species although Cu valence was entirely +1 after the treatment. It was found that the reduction eliminates the remaining +2 species. It is important to distinguish superconductivity-correlated behavior from simple doping dependence and oxygen stoichiometry dependence.

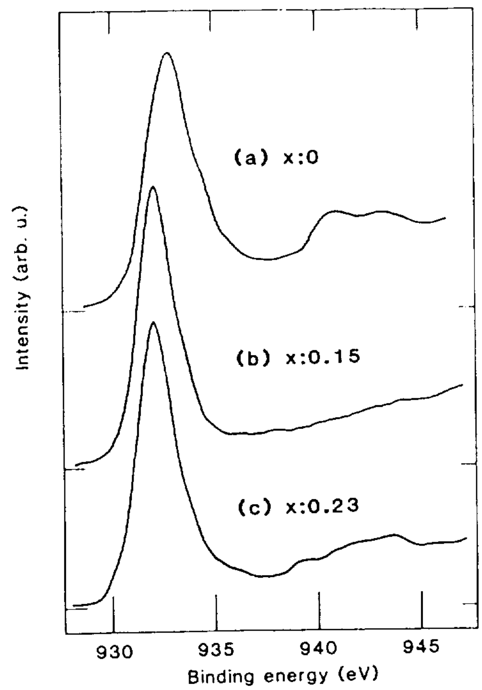

Fig.6. The Cu $2p_{3/2}$ spectra of the $Nd_{2-x}Ce_xCuO_4$ thin films.

4. Bi-BASED THIN FILMS

4.1 LANTHANOID SUBSTITUTED Bi-Sr-Ln-Cu-O THIN FILMS

For the lanthanoid element, we chose a series of (Nd,Ce) similar to the electron-doped $(Nd,Ce)_2CuO_4$ system. The construction of crystal phases in Bi-Sr-(Nd,Ce)-Cu-O films on MgO (100) substrates was investigated. Ordinarily, 2-2-1-2 phase was easily obtained in this system when the deposition was carried out at the substrate temperature of 600-700°C, or amorphous films deposited at 400°C were annealed at a temperature of 800-900°C. In this 2-2-1-2 phase, lanthanoid elements are supposed to occupy the intermediate site between two CuO_2 planes. When the annealing procedure of amorphous film was carried out at higher temperature (1100°C), other phase was created. This crystal structure was found to be 2-2-2-2 phase recently discovered by Tokura et al. [11], where two CuO_2 planes are separated by two lanthanoid layers and a oxygen layer. Figure 7

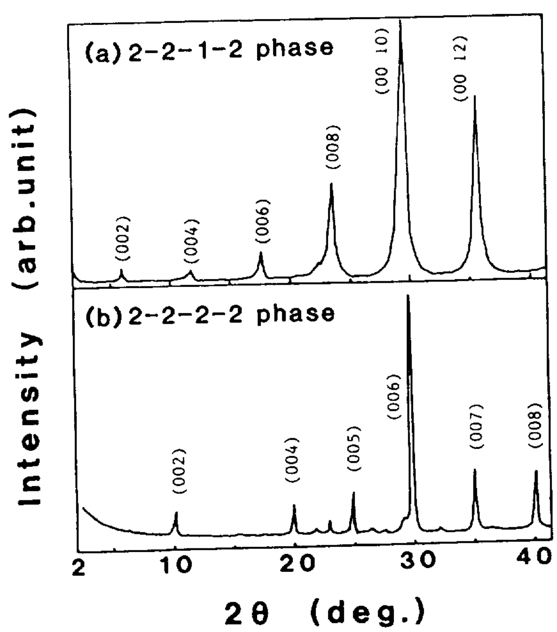

Fig.7. X-ray diffraction patterns for the Bi-Sr-(Nd,Ce)-Cu-O thin films.

shows the X-ray diffraction patterns of Bi-Sr-(Nd,Ce)-Cu-O thin films with (a) 2-2-1-2 phase and (b) 2-2-2-2 phase. c-axis orientation normal to the substrates was confirmed in both films, and lattice constant c was estimated to bi 3.02 nm for 2-2-1-2 phase and 1.77 nm for 2-2-2-2 phase. Although we also tried to prepare Bi-Sr-Ln-Cu-O system with three CuO_2 planes, it seems to be very difficult when lanthanoid elements were doped in the Bi-system.

Detailed experiments were done on the 2-2-1-2 phase of Bi-Sr-(Nd,Ce)-Cu-O system. Figure 8 shows the relation between Ce content x and lattice constant c of the films. The lattice constant c lengthens with the increase of content x, i.e. substitution of Ce for Nd. In the case of $Nd_{2-x}Ce_xCuO_4$ superconducting system, where the valence of Ce is +4, the lattice constant c shrinks with Ce content x [6]. The results shown in Fig.8 is opposite to the case for the electron carrier type superconductor of $Nd_{2-x}Ce_xCuO_4$ system. From the consideration of ion radius, where $Ce^{4+}<Nd^{3+}<Ce^{3+}$, the valence of Ce in the 2-2-1-2 phase of Bi-Sr-(Nd,Ce)-Cu-O is supposed to be +3. This speculation agreed with the result of XPS study. The valence of the site between two CuO_2 planes seems not to exceed +3.

Figure 9 shows the room-temperature resistivity of the Bi-Sr-(Nd,Ce)-Cu-O films at various x. The resistivity decreases with the Ce content x, which may indicate that the carrier is supplied by doping of Ce to insulating $Bi_2Sr_2NdCu_2O_y$ structure. Post-treatment study showed that the reducing treatment did not change or somewhat increase the resistivity, on the other hand the oxidizing treatment decreased resistivities of the films for every Ce content x remaining the same tendency. Since the valence of Ce in the $Bi_2Sr_2(Nd,Ce)Cu_2O_y$ system was found to be same as Nd, +3, it is unlike to supply charge carrier by Ce doping. More detailed research such as oxygen stoichiometry is desired to elucidate the decrease of the resistivity with Ce content.

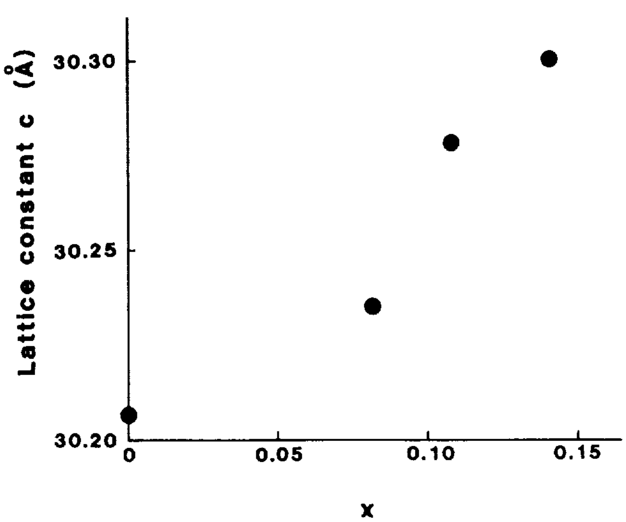

Fig.8. The relation between Ce content x and lattice constant c for the $Bi_2Sr_2Nd_{1-x}Ce_xCu_2O_y$ films.

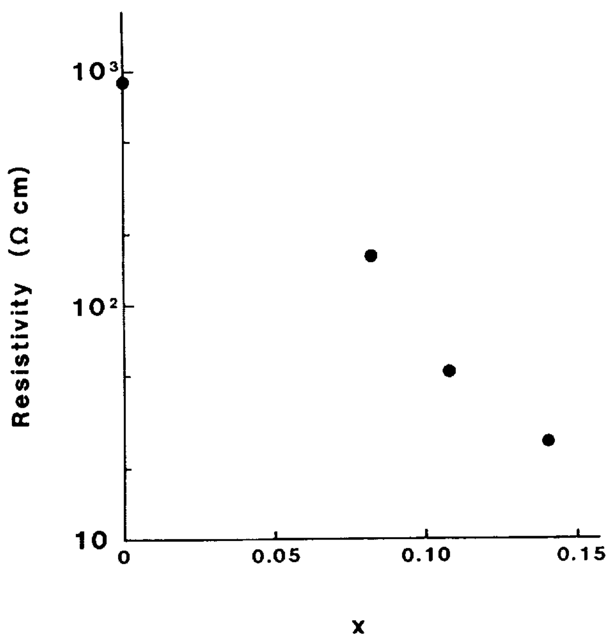

Fig.9. The relation between Ce content x and the resistivity for the $Bi_2Sr_2Nd_{1-x}Ce_xCu_2O_y$ films.

4.2 Bi-Sr-Cu-O THIN FILMS

The another advantage of the thin-film samples is construction of metastable state since novel crystal structures of unequilibrium state are sometimes created in thin films. In the course of the experiment of the Bi-Sr-Ln-Cu-O system, we dealt with no lanthanoid composition. The Bi-Sr-Cu-O system is known as the 10 K superconductor in the $Bi_2Sr_2CuO_y$ (2-2-0-1) phase [12,13]. New superconducting phases were investigated in this simple Bi-Sr-Cu-O system.

Thin films were prepared onto MgO (100) substrates. When the substrate temperature was elevated at around 600-650°C, new crystal structure having a long c-axis was created in addition to the ordinary 2-2-0-1 phase. By adjusting the film composition and the substrate temperature, almost single phase of the new structure was obtained at the substrate temperature of 630°C [14]. The chemical composition of the films was found to be nearly Bi:Sr:Cu=2:3:2.5. Figure 10 shows the X-ray diffraction pattern of the film. Bismuth-oxide layered structure with c-axis orientation normal was confirmed. The lattice constant c was estimated to be 3.12 nm, which was fairly larger than 2-2-0-1 phase (2.46 nm) and suggested the creation of 2-2-1-2 phase in the simple Bi-Sr-Cu-O system. By the present sputtering method, the metastable phase such as the 2-2-1-2 structure in the Bi-Sr-Cu-O system was successfully formed.

The as-deposited films exhibited a semiconductor-like temperature dependence of the resistivity. In order to improve the electric properties, films were heat-treated at 750°C for 30 min in oxygen. Figures 11 shows the

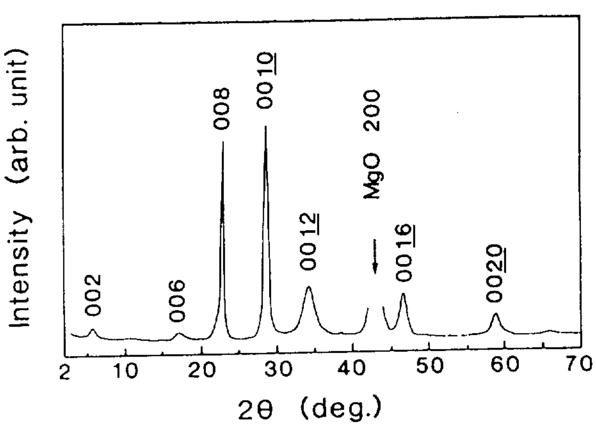

Fig.10. X-ray diffraction pattern for the Bi-Sr-Cu-O thin film with 2-2-1-2 phase.

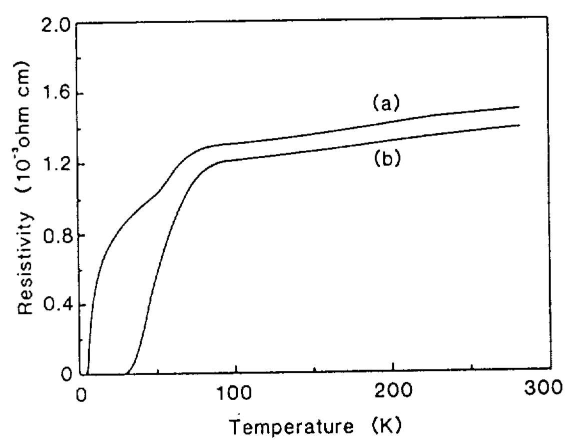

Fig.11. Temperature dependence of the resistivity for the Bi-Sr-Cu-O thin film with 2-2-1-2 phase.

temperature dependence of the resistivity. The film of the new phase exhibited superconductivity with an onset temperature as high as 80 K. However, the transition width is not so sharp, and the zero-resistance state was achieved below 29 K.

Transmission electron microscopy (TEM) analyses operated at 350 kV were carried out. Figure 12 shows the lattice image of the film including c axis. The major length between Bi_2O_2 layers is 1.5 nm, which is consistent with the X-ray diffraction pattern. Intergrowths of the other units were also observed in the figure (1.2 nm and 1.9 nm). The 1.2-nm phase is the conventional $Bi_2Sr_2CuO_y$ which has a single CuO_2 plane between Bi_2O_2 layers. The phases with the units of 1.5 nm and 1.9 nm are similarly considered to have double and triple CuO_2 planes between Bi_2O_2 layers in the Bi-Sr-Cu-O system, respectively. The broad superconducting transition may be due to the random intergrowth of multiphases with different CuO_2 planes. Figure 13 shows the electron diffraction pattern taken with incidence [001] showing the a^*-b^* reciprocal lattice of the subcell with a=b=0.54 nm. The long period modulation of 2.6 nm which corresponds to 4.8b is observed along b^* as commonly observed in the $Bi_2Sr_2CuO_y$ or $Bi_2Sr_2CaCu_2O_y$ system.

In this experiment, there remain several subjects; for instance, occupancy of oxygen in the intermediate Sr layer, optimization of annealing, or formation of the structure with more than three CuO_2 planes. Further investigation is expected to discuss the superconductivity in this simple Bi-Sr-Cu-O system.

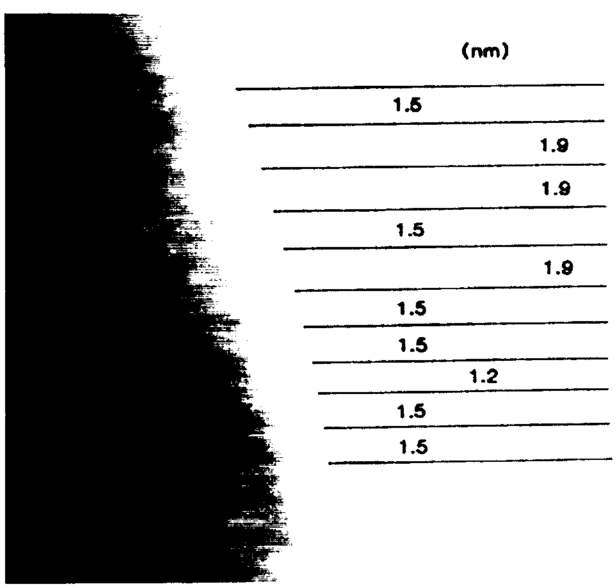

Fig.12. Lattice image of the Bi-Sr-Cu-O thin film including c-axis.

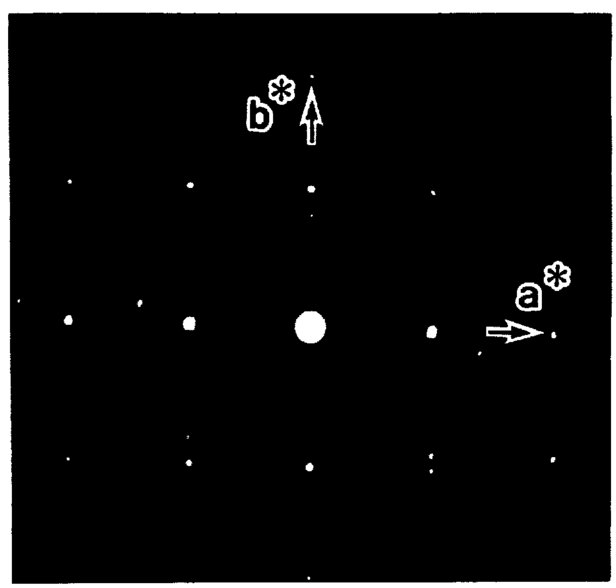

Fig.13. Electron diffraction pattern of the Bi-Sr-Cu-O film with 2-2-1-2 phase.

5. SUMMARY

By taking advantage of thin film samples, several experiments have been carried out. Thin films of electron-doped-type $(Nd,Ce)_2CuO_4$ were prepared with excellent quality and their superconducting, optical, and XPS properties were revealed. Lanthanoid substituted Bi-system of Bi-Sr-(Nd,Ce)-Cu-O films were firstly prepared and conditions of phase creation such as 2-2-1-2 and 2-2-2-2 phases were found. Moreover, metastable 2-2-1-2 phase were obtained in simple Bi-Sr-Cu-O system by the thin-film processing and 80-K superconductivity was confirmed. The present thin-film processing will be one of the most useful methods to prepare new superconducting phases, which will give much information on the nature of cuprate superconductors.

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