International Symposium on Lattice Effects in Cuprate High Temperature Superconductors IOP Publishing
Journal of Physics: Conference Series **108** (2008) 012041 doi:10.1088/1742-6596/108/1/012041

Epitaxial growth of $Gd_{2-x}Ce_xCuO_4$ thin films

Y Krockenberger[1,3], **J Kurian**[1,3], **M Naito**[2,3] **and L Alff**[1]

[1]Institute of Materials Science, TU Darmstadt, Petersenstr. 23, 64287 Darmstadt, Germany
[2]Tokyo University of Agriculture and Technology (TUAT), 2-24-16, Naka-cho, Koganei, Tokyo 184-8588, Japan
[3]NTT Basic Research Laboratories, NTT Corporation, 3-1 Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan

E-mail: yoshiharu.krockenberger@aist.go.jp

Abstract. We have grown (00l)-oriented thin films of $Gd_{2-x}Ce_xCuO_4$ with cerium composition $0 < x < 0.2$ by state-of-the-art reactive molecular beam epitaxy and characterized them by x-ray diffraction and transport measurements. A systematical change in the *c*-axis length upon cerium doping indicates that single-phase films were obtained for the whole doping range. Based on a log p_{O2} − 1/T phase diagram in combination with reflection high energy electron diffraction (RHEED), phase stability has been determined in order to achieve optimized reduction conditions. $Gd_{2-x}Ce_xCuO_4$ thin films even after controlled reductions treatment did not show superconductivity in the whole range of Ce concentration studied. However, the room temperature resistivity of optimally reduced $Gd_{2-x}Ce_xCuO_4$ thin films shows a minimum at around $x_{Ce} = 0.16$. Our results on the growth and characterization of $Gd_{2-x}Ce_xCuO_4$ thin films on (100) SrTiO3 substrates are described in detail.

1. Introduction

Layered materials attract high attention due to there fascinating physical properties. Especially, layered transition metal oxides where the transition metal ion copper has gained high interest due to high superconducting transition temperatures. The phase diagram of cuprate superconductors is commonly split into hole- and electron doped cuprates [11]. In hole doped cuprates, copper is a six fold coordinated ion while it is four fold coordinated in the case of electron doped cuprates. While the family of hole doped cuprates is large, i.e., $La_{2-x}Sr_xCuO_4$, $RE_1Ba_2Cu_3O_7$, Bi-2212, Bi-2202, Bi-2223, Hg-1234, Hg-1245, and so on, only two structure types are known in the case of electron doped cuprates ($RE_{2-x}(Ce,Th)_xCuO_4$ with RE = La, Pr, Nd, Sm and Eu, and $Sr_{1-x}RE_xCuO_2$). Unlike the hole doped cuprates which belong to the K_2NiF_4 structure, the electron doped cuprates crystallize in the Nd_2CuO_4 or T' structure. This structure type is thermodynamically stable for a certain range of tolerance factor, which has been shown by Bringley *et al.* [4]. The upper threshold lies between La and Pr, where the T structure (that is the structure of the hole doped $La_{2-x}Sr_xCuO_4$) becomes thermodynamically favorable. Whereas the lower threshold lies near Dy which forms $Dy_2Cu_2O_5$ structure. However, this structure does not preserve the tetragonal symmetry but becomes monoclinic. On the other hand, crystal structures with a high degree of symmetry are preferable for superconductivity. As it is shown in the report by Bringley et al., the case where RE = Gd in $RE_{2-x}Ce_xCuO_4$ is just at the borderline between the T'- and $Dy_2Cu_2O_5$ structures. Earlier reports on $Gd_{2-x}Ce_xCuO_4$ already indicate, that the reduced symmetry [15] of the σ' structure which would probably leed to a magnetic pair breaking effect [14] or ferrimagnetic instabilities [9, 16, 17, 18, 19, 20, 21, 22]. However, since Gd is smaller than Eu, effective removal of apical oxygen while consequently protecting the T0 structure might play a key role in investigating the properties of $Gd_{2-x}Ce_xCuO_4$. This fact is related to the small in-plane lattice constant of the tetragonal phase of $Gd_{2-x}Ce_xCuO_4$ which in turns provides a too small electron concentration for the appearance of superconductivity [10].

2. $Gd_{2-x}Ce_xCuO_4$

It is well known, that the growth of epitaxial thin films is a powerful tool for investigations of certain crystal structures. Since reactive molecular beam epitaxy is a powerful tool for the epitaxial stabilization of electron doped cuprate superconductors which have same crystal structure [5], thin films of $Gd_{2-x}Ce_xCuO_4$ have been deposited by this method on (001) $SrTiO_3$ substrates. Since superconductivity was first reported on electron doped cuprates by Tokura et al. [1] the striking difference to their hole doped analogues cuprate superconductors is that superconductivity can be only achieved after an additional oxygen reduction treatment. In the electron-doped (n-doped) cuprate system $RE_{2-x}Ce_xCuO_4$, Ce^{4+} or Th^{4+} partially replaces the rare earth ion (RE^{3+}) thereby introducing electrons into the CuO_2 plane [2]. Additionally, as mentioned earlier, a crucial structural difference accompanies the n-type cuprates compared to their hole doped analogues: n-type cuprates crystallize in the Nd_2CuO_4 [3] or T' structure causing a four-fold coordination of copper. However, doping alone is insufficient to obtain superconductivity since oxygen stoichiometry and oxygen reduction plays a vital role in inducing superconductivity. In thin film processing the oxygen reduction is done by annealing at vacuum chamber pressures below 10−9 Torr. Oxygen seriously affects not only Tc, but also many other properties like resistivity or the Hall coefficient.

2.1. Growth of $Gd_{2-x}Ce_xCuO_4$ thin films

Thin films of electron doped cuprates are primarily investigated by the Nd-Ce-Cu-O or the Pr-Ce-Cu-O system. So far, there are no reports of growth of thin films of $Gd_{2-x}Ce_xCuO_4$ in the literature. As it is well known, materials grown by thin film synthesis, crystal structures can be stabilized which are not available in bulk form. It was mentioned earlier that $Gd_{2-x}Ce_xCuO_4$ tends to turn away from forming the T' structure due to the small ionic radius of Gd^{3+}. However, when grown as a thin films at low enough growth temperatures, the T0 structure can be conserved. Therefore, thin films of $Gd_{2-x}Ce_xCuO_4$ are an exigency for the understanding of the underlying physics and the absence of superconductivity if it holds also for thin films. In the present study, the films have been deposited on (001)$SrTiO_3$ substrates. Compared to bulk single crystal data, an in-plane tensile strain should occur since the in-plane lattice of $SrTiO_3$ is larger (a = 3.905Å). Thin films of *c*-axis oriented $Gd_{2-x}Ce_xCuO_4$ were grown by reactive molecular beam epitaxy on (100) oriented $SrTiO_3$ substrates. A custom designed ultra high vacuum chamber with base pressure of $\approx 10^{-9}$ Torr has been used. Stoichiometry control was achieved using electron impact emission spectroscopy which is described elsewhere [8]. Inductively coupled plasma (ICP) analysis have been performed in order to avoid deviations from the cerium content and to ensure, that the thin films do not have a cerium gradient along the growth direction. The substrates were heated radiantly and the temperature was controlled by a thermocouple and calibrated by an optical pyrometer. The films were grown under O_3 and the background pressure during growth was $2 \cdot 10^{-6}$ Torr. Annealing (removal of apical oxygen) was performed *in situ*, at 580°C at 10^{-9} Torr base pressure. According to results of Mang et al. [7] too strong reduction conditions carried out on $Nd_{2-x}Ce_xCuO_4$ causes decomposition and formation of $(Nd,Ce)_2O_3$ [7] and Cu_2O (even the formation of bixbyite structured $NdCuO_2$ [6] is possible). Since the growth and the annealing of the samples are assisted by RHEED, the formation of decomposition products can be detected even when it starts and therefore circumvented. By aid of RHEED, the thermodynamic stability region in the log $p_{O_2} - 1/T$ phase diagram has been determined. In the present study the typical film thickness was 1000 Å.

2.2. *Crystal structure characterization*

The structure of the $Gd_{2-x}Ce_xCuO_4$ films were examined by X-ray diffraction (XRD) using a Rigaku x-ray diffractometer with Cu Kα radiation and Fig. 1 shows the $2\theta-\theta$ XRD pattern of $Gd_{2-x}Ce_xCuO_4$ (x = 0.15) thin film grown on (100) $SrTiO_3$ substrate. In the XRD pattern (Fig. 1), all the peaks except the characteristic peaks of $SrTiO_3$ are that of (00l) reflections of $Gd_{2-x}Ce_xCuO_4$, indicating the single phase nature of the films. We have grown single phase thin films of $Gd_{2-x}Ce_xCuO_4$in the whole cerium concentration range of x = 0 to 0.2. The variation of *c*-axis lattice parameters of $Gd_{2-x}Ce_xCuO_4$ films with cerium content, x = 0 to 0.2, is presented in Fig. 2. The *c*-axis lattice parameters are calculated by the Nelson-Riley method.

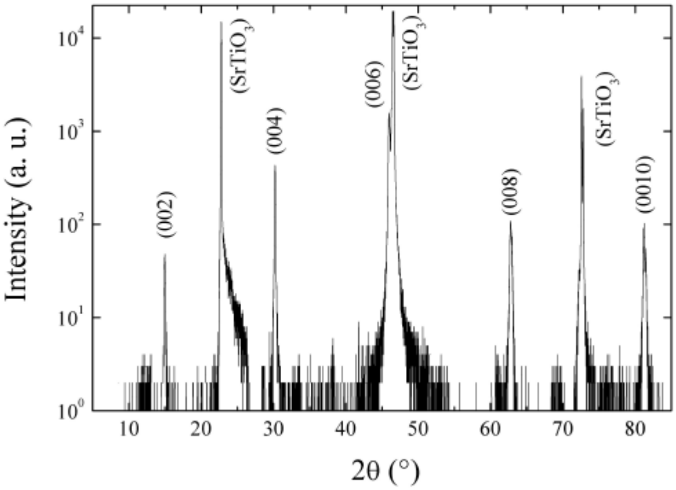

Figure 1. X-ray diffraction pattern of a $Gd_{1.85}Ce_{0.15}CuO_4$ thin films grown on (001)$SrTiO_3$.

2.3. *Transport properties*

The electrical transport measurements of $Gd_{2-x}Ce_xCuO_4$ thin films were studied by standard four-probe technique. Figure 3 shows the resistivity vs. temperature of $Gd_{1.85}Ce_{0.15}CuO_4$ thin film grown on $SrTiO_3$. Even though the room temperature resistivity of the $Gd_{2-x}Ce_xCuO_4$ thin films showed a decrease with increase in cerium concentration up to x = 0.15, superconductivity was not observed for any samples studied in the whole cerium concentration range. For the $Gd_{2-x}Ce_xCuO_4$ films with cerium concentration of x = 0.16 the room temperature resistivity was 1.2 mΩcm. However, it should be noted that metallic behavior is observed between room temperature and ≈70K where the resistivity value reaches 0.7 mΩcm. For lower temperatures the resistivity value increases and shows semiconducting behavior. Figure 4 shows the room temperature resistivity values vs. cerium content for $Gd_{2-x}Ce_xCuO_4$ thin film grown on (100)$SrTiO_3$ in the doping concentration range $0 \leq x \leq 0.2$. For the samples used above, the reduction treatment has been optimized according to thermodynamic stability conditions. The room temperature resistivity subsequently decreases with increasing cerium concentration up to x≈0.16. This behavior is in contrast to the case of thorium doping [12, 13], where an increase of the room temperature resistivity has been observed. However, it is not clear whether the thorium doped samples have been treated by an annealing procedure. Here, it was possible to anneal thin films in a way that no decomposition products are formed. It can be seen that the absolute value decreases by about two orders of magnitude from the un-doped compound towards x≈0.15. The

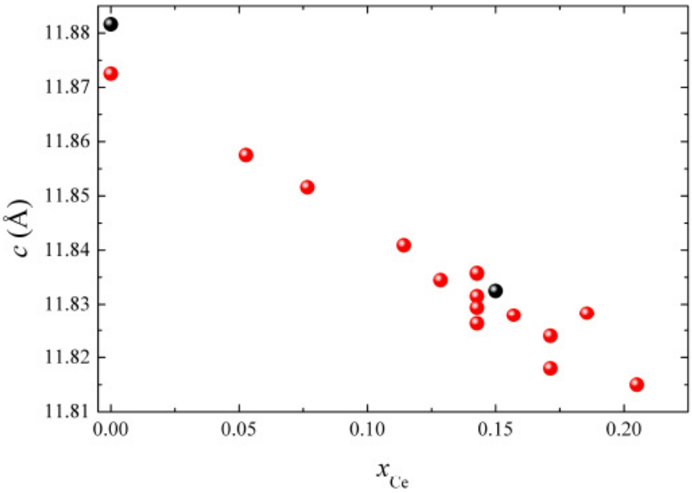

Figure 2. *c*-axis lengths of $Gd_{2-x}Ce_xCuO_4$ thin films grown on (001)$SrTiO_3$ (red dots). For comparison data points from Uzumaki (black dots) are included.

reduction of the absolute value of resistivity is accompanied by two processes. First, since Ce is added, the antiferromagnetic background dilutes and the mobility of the charges enhances. Secondly, with increasing cerium concentration, apical oxygen can be more easily removed during the annealing process. Since apical oxygen might be considered as a scattering center, its removal enhances the mean free path lengths of the electrons and therefore the absolute resistivity value decreases more. However, at the present stage it is not possible to independently determine to which degree both process reduce or increase the conductivity of the material. Compared to previous studies it seems to be an unique effect to all electron doped cuprate superconductors.

2.4. *Impact of apical oxygen*

In order to investigate the effect of oxygen on the different properties in depth, we thought of approaching the problem from another angle, i.e., try to feed as much oxygen as possible to the cuprate. We speculate, that an enhanced occupation of apical sites of copper induces insulating behavior. More copper will become partially six-fold coordinated and therefore leading to an increase in the ionic radius of copper. For this experiment, a custom designed quartz reactor was used. Ozone was produced by a silent discharge generator with typical ozone concentration of approx. 32%. A feed-through quartz-tube mounted directly above the sample ensured, that the sample is adequately supplied by fresh ozone. Samples were mounted on a sapphire plate heated by a custom designed Pt-Rh heater. After 24 h at 400^{o}C samples were cooled to roomtemperature at 2K/min. It was found that, there is an increase of about 0.14 Å (for $x = 0$) of *c*-axis length after the oxidizing treatment, which is drastic. Figure 5 shows the variation of resistivity with temperature for undoped Gd_2CuO_4 thin film grown on (100)$SrTiO_3$ substrate one after reduction treatment (red curve) and the other after ozone annealing (black curve). The absolute room temperature resistivity value increased by one order of magnitude after the ozone annealing treatment..

2.5. *Summary*

Thin films of T’ $Gd_{2-x}Ce_xCuO_4$ have been grown for the first time. We have successfully grown single phase T’ $Gd_{2-x}Ce_xCuO_4$ in the cerium concentration range $0 < x < 0.2$ by reactive molecular beam epitaxy on (100)$SrTiO_3$ substrates. Although it has been found that the general trend is similar to that observed for other T0 compounds, where the absolute resistivity value decreases upon increasing Ce concentration, no superconductivity has been observed. Moreover, also various reduction recipes have been utilized in order to induce superconductivity. The absence of superconductivity might be related

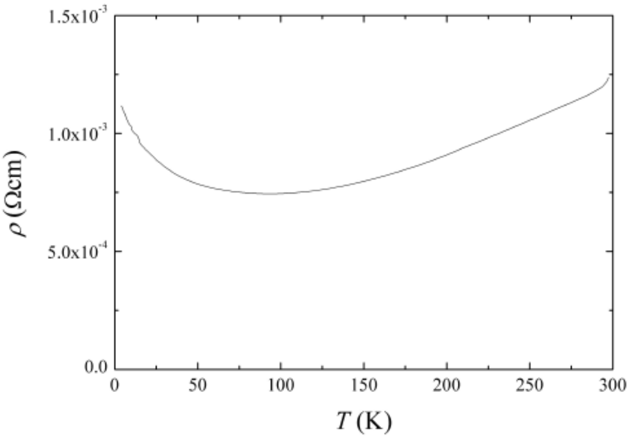

Figure 3. Resistivity vs. temperature of a $Gd_{1.85}Ce_{0.15}CuO_4$ thin film grown on (001)$SrTiO_3$.

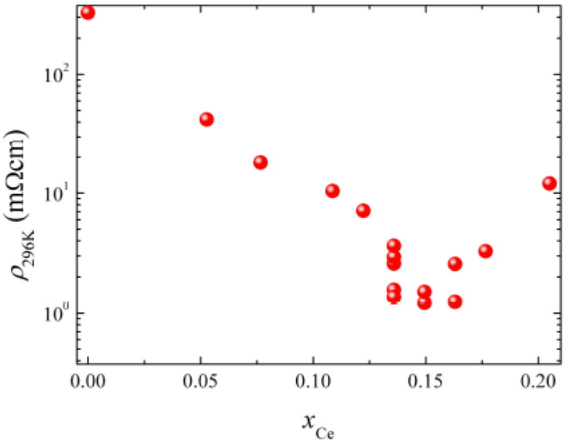

Figure 4. Room temperature resistivity values of $Gd_{2-x}Ce_xCuO_4$ thin films grown on (001)$SrTiO_3$. For some cerium concentrations various data points denote various reduction conditions.

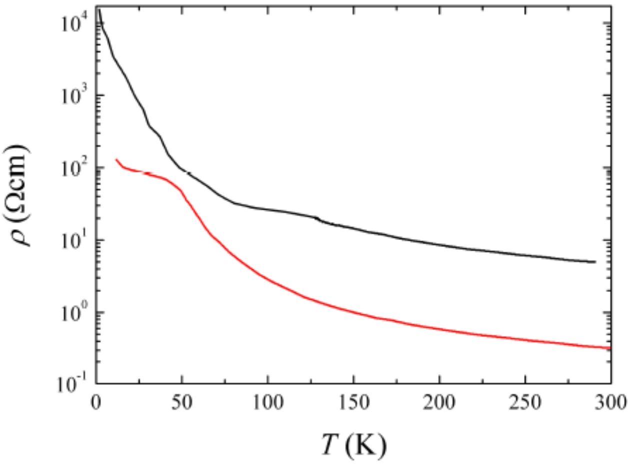

Figure 5. Resistivity vs. temperature of a Gd_2CuO_4 thin films grown on (001)$SrTiO_3$. The red curve was obtained after optimal reduction treatment whereas the black curve was obtained after an excessive ozone treatment.

to the fact that the used substrate does not provide the necessary template to introduce the required Cu–O bond length which is found in superconducting T' cuprates. Or the growth temperature might have been to high thereby creating intrinsic oxygen deficiency in the CuO_2 plane. Recently, Naito et al. [23] reported the occurrence of superconductivity even on RE_2CuO_4 samples without cerium. These samples have been prepared by MOD at much lower growth temperatures. This might indicate, that the key for achieving superconductivity might also be associated with the quality of the CuO_2 plane itself. Since the absolute resistivity value increased by one order of magnitude after the ozone annealing treatment, and moreover, also the *c*-axis length increased considerably, the influence of apical oxygen might be considered as a scattering center reducing the mean free path lengths of electrons.

Acknowledgements

The authors would like to thank H. Yamamoto, A. Tsukuda, D. Manske, S. Karimoto, C. Bernhard, G. Cristiani and P. Yordanov for prolific discussions.

References

[1] Y. Tokura, H. Takagi and S. Uchida, *Nature* (London) 337, 345 (1989)
[2] H. Takagi, S. Uchida and Y. Tokura, *Phys. Rev. Lett.* 62, 1197 (1989)
[3] H. Mueller-Buschbaum and W. Wollschlaeger, *Z. Anorg. Allg. Chemie* 414, 76 (1975)
[4] J. F. Bringley, S. S. Trail and B. A. Scott, *J. Solid State Chem.* 87, 402 (1990)
[5] M. Naito, S. Karimoto and A. Tsukada, *Supercond. Sci. Technol.* 15, 1663 (2002)
[6] J. Hauck, K. Bickmann and K. Mika, *Supercond. Sci. Technol.* 11, 63 (1998)
[7] P. Mang, S. Larochelle, A. Mehta, O. P. Vajk, A. S. Erickson, L. Lu, W. J. L. Buyers, A. F. Marshall, K. Prokes, and M. Greven, *Phys. Rev. B* 70, 094507 (2004)
[8] M. Naito and H. Sato, *Appl. Phys. Lett.* 67, 2557 (1995)
[9] A. Butera, A. Caneiro, M. T. Causa, L. B. Steren, R. Zysler, M. Tovar and S. B. Oseroff, *Physica C* 160, 341 (1989)
[10] A. Manthiram and Y. T. Zhu, *Physica C* 226, 165 (1994)
[11] L. Alff, Y. Krockenberger, B. Welter, M. Schonecke, R. Gross, D. Manske and M. Naito, *Nature* (London) 422, 698 (2003)
[12] T. Kenjo and S. Yajima, *Bull. Chem. Soc. Japan* 46, 2619 (1973)
[13] T. Kenjo and S. Yajima, *Bull. Chem. Soc. Japan* 50, 2847 (1977)
[14] A. Matsushita, S. Uji and T. Matsumoto, *Solid State Comm.* 87, 321 (1993)
[15] M. Braden, W. Paulus, A. Cousson, P. Vigoureux, G. Heger, A. Goukassov, P. Bourges and D. Petitgrand, *Europhys. Lett.* 25, 625 (1994)
[16] A. Roucoa, J. L. García-Muñoza, F. Péreza, J. M. Navarroa, A. Fuertesa, S. Piñola, X. Obradorsa and M. Tovar, *Physica C* 235–240, 1569 (1994)
[17] J. Mira, J. Rivas, J. Mahía, C. Vázquez-Vázquez, M. A. López-Quintela, A. Butera, M. Tovar and S. B. Oseroff, *Europhys. Lett.* 34, 623 (1996)
[18] S. G. Kaplan, T. W. Noh, A. J. Sievers, S-W. Cheong and Z. Fisk, *Phys. Rev. B* 47, 5300 (1993)
[19] J. Mira, J. Castro, J. Rivas, D. Baldomir, C. Vázquez-Vázquez, J. Mahía, A. López-Quintela, D. Fiorani, R. Caciuffo and D. Rinaldi, *J. Appl. Phys.* 76, 7034 (1994)
[20] T. Ishii and A. Matsuda, *Solid State Chem.* 75, 765 (1990)
[21] A. Butera, M. Tovar, S. B. Oseroff, Z. Fisk, *Phys. Rev. B* 52, 13444 (1995)
[22] J. Mira, J. Rivas, A. Butera, L. B. Steren, J. M. García-Beneytez and M. Vázquez, *J. Appl. Phys.* 87, 5911 (2000)
[23] M. Naito, International symposium on lattice effects in high temperature superconductors, Tsukuba, Japan (2007)