Pulsed - laser deposition of superconducting $Nd_{1.85}Ce_{0.15}Cu_{4-\delta}$ thin films and their structural examinations

Ariando[1,2] and Darminto[3,*]

[1]*Low Temperature Division, Faculty of Science and Technology, and MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.*
[2]*Departemen Fisika, FMIPA, Institut Teknologi Bandung, Jl. Ganesa 10, Bandung 40132*
[3]*Jurusan Fisika, FMIPA, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111*

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Abstract

Thin films of electron - doped superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ have been deposited on (100) $SrTiO_3$ substrates at 680 - 840°C using pulsed - laser deposition. The deposition process was conducted in flowing oxygen with the rate of 25 ml/min and the pressure of 0.25 mbar. The in-situ post-annealing treatments in vacuum (down to 10^{-7} mbar) for several minutes at deposition and/or lower temperatures were given to induce superconductivity on the films. The best quality of films with Tc of about 20 K, smooth surface, nanometer-sized grains and average roughness of 3.5 nm have been produced by the growing film at 820°C followed by annealing at 750°C in vacuum for 5 minutes.

KEYWORDS: thin-film, superconductivity, NCCO

I. INTRODUCTION

The family of $Re_{2-x}Ce_xCuO_{4-\delta}$ compounds with Re = Nd, Pr, La, Sm, Eu and Gd (rare-earth elements) are known to be electron-doped superconductors of the 214-system, which are not less interesting than their hole-doped counterparts, such as $La_{2-x}A_xCuO_4$ with A = Sr or Ba. The issue of superconducting order parameter pairing symmetry of $Nd_{2-x}Ce_xCuO_{4-\delta}$ (NCCO), also $La_{2-x}Ce_xCuO_4$ (LCCO) and $Pr_{2-x}Ce_xCuO_4$ (PCCO), from s-wave [1] to d-wave [2] character, for example, has led to a long debate for more than a decade. Meanwhile, the superconductivity itself of these compounds strongly depends on both Ce (x) and oxygen (δ) content, which can basically act as dopants [3]. The highest critical temperature Tc of around 23 K for the NCCO polycrystalline pellet is achieved with x = 0.15 and δ = 0.04 [4]. This doping state is considered to be optimal.

The as-deposited NCCO films grown in oxygen atmosphere by pulsed-laser deposition (PLD) method are generally non-superconducting, and have to be reduced to achieve superconductivity, which is attributed to the removal of excess interstitial oxygen on the apical sites [5] by annealing films in vacuum. The oxygen reduction carried out in long duration, on the other hand, creates significant defects on the film's surface, leading to a drastic increase of surface roughness due to deficiency of copper [6], being disadvantageous for devices technology, mainly Josephson junction-based devices [7]. To solve this contradictive situation of the film fabrication, a thorough control has to be performed on the post-annealing process to result in superconducting film with low average roughness (less than 10 nm).

In this paper we report our activities in fabricating superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ thin films by means of PLD technique on $SrTiO_3$ (STO) substrates. The high quality films were successfully grown at relatively higher deposition temperature (up to 840°C) and then annealed in vacuum at somewhat lower temperature as suggested recently [8]. To optimize the deposition and annealing process in producing superconducting NCCO films with a good surface, characterizations employing X-ray diffractometer (XRD), scanning electron microscope (SEM) as well as atomic force microscope (AFM) would be described and discussed. Although there have already been many reports on the NCCO films in almost fifteen years since this compound was discovered, to the best of our knowledge, the studies focusing on the micro-structural aspects have so far been relatively rare.

*E-MAIL: darminto33@yahoo.com

II. EXPERIMENT

The NCCO films were grown by PLD using the target having stoichiometric molar composition of $Nd_{1.85}Ce_{0.15}CuO_y$ and the diameter of 2.5 cm. The (100) STO substrates of 5x5 mm^2 or 5x10 mm^2 were used and fixed on the heater/substrate holder placed in the distance of 50-55 mm from the target. A pulsed laser beam generated by a Lamda - Physik XrF Excimer Laser System with = 248 nm was utilized for the deposition passed through a window to the target using a lens with a focal length of 45 cm. The laser beam having fluence of 2.5 J/cm^2 was focused on the target with spot size of 3.6 mm^2. Energies up to 650 mJ and repetition rate of 4 Hz were reached in a pulsed mode. Background pressures in the homemade vacuum PLD chamber were below 10^{-7} mbar. Deposition gases such as O_2 and Ar are provided and their pressure can be varied controllably from 10^{-4} to 0.5 mbar using mass-flow controllers and variable valves system. The deposition process in flowing oxygen atmosphere with a rate of 25 ml/min and pressure of 0.25 mbar was conducted at various temperatures between 680°C and 840°C. The in-situ post-annealing of the as-deposited film in vacuum (10^{-5} - 10^{-7} mbar) for several minutes was then done at the same temperature as and/or at lower temperature than deposition one and followed by an in-chamber cooling. A pre-ablation procedure to remove any attached impurities on the target is always performed before the deposition process using laser beam with the same energy as that of deposition and repetition rate of 10 Hz. The image of laser plasma created between the target and the substrate is depicted in Fig. 1. With the mentioned experimental parameters, the NCCO grew on the STO substrate with the rate of 0.83 Å/pulse. In this experiment we deposited film with the thickness of about 150 nm.

Discussing further the substrate, we have chosen the STO one having cubic crystal structure with lattice parameter a = 3.905 Å which is closer to that of NCCO unit cell with a = 3.945 Å, compared to other substrates, such as $YAlO_3$ (a = 3.715 Å), $LaAlO_3$ (a = 3.793 Å), NdGaO3 (a = 3.860 Å) and MgO (a = 4.216 Å) [9]. It favors an epitaxial growth and therefore ensures alignment of the crystal axes of NCCO and the substrates. After a cleaning step in an ultrasonic bath using acetone and alcohol, the STO substrates were etched using an HF solution [10] to obtain a single TiO_2 terminated surface. The substrates were then annealed in flowing oxygen with a rate of 150 ml/min for 1.5 hours at 950°C. This procedure is expected to result in a flat substrate surface with only unit cell steps. The sketch of crystalline axes of STO substrate and the deposited film is shown in Fig. 2, while a photo of the grown NCCO film on a 5x10 mm^2 STO substrate is given in the inset.

Characterizations to determine Tc was done by measuring resistance (R) vs. temperature (T), whereas the XRD measurements were performed to analyze the c-axis lattice parameter, the phase purity and the alignment of film growth. The film's surface morphology was studied by employing SEM observation focusing on the surface damage due to post-annealing in vacuum. The grain structure, its homogeneity, size and average roughness were examined by an AFM.

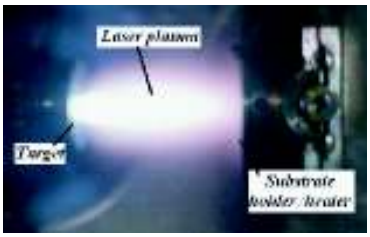

FIG. 1: A laser plasma in the PLD chamber, generated by a laser beam on the target.

III. RESULTS AND DISCUSSIONS

Presented in Fig. 3a and 3b are the XRD spectra of the NCCO films deposited at 780°C and 820°C respectively. In general, the film has epitaxially grown almost exactly parallel to the c-axis which is perpendicular to the substrate surface, as attributed by the appearance of the (00l) diffraction peaks, with l = even numbers. We indexed the diffraction pattern to a tetragonal T' structure with space group I4/mmm [11] to yield the c lattice parameter of 12.09 and 12.06 Å respectively for both spectra, being nicely comparable to c = 12.08 Å for the NCCO crystalline bulk [12]. Rocking curves through (006) plane of both films give a typical full width at half maximum (FWHM) of 0.13° and 0.15° (comparable to 0.11° [12]). As reported in earlier works [13], additional peaks at 2 = 32.5° and 68.2° are clearly observed as well from the spectra. These peaks are associated with diffraction planes of (110) and (220), implying the growth of non-c-aligned

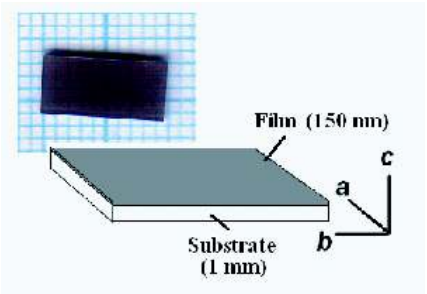

FIG. 2: Illustration of crystal axes of the STO substrate and the grown film. *Inset*: the as-deposited NCCO film on a 5x10 mm^2 STO substrate.

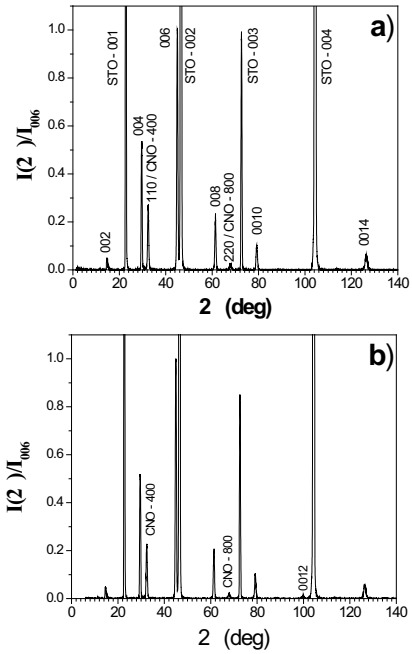

FIG. 3: XRD spectra for the NCCO films deposited at : a). 780° and b). 820°. The (hkl) indexes stand for deposited film, the STO - (hkl) for substrate, and the CNO - (hkl) for impurity phase.

components of the films mainly deposited at lower temperature below 750°C [14]. In the mean time, from the TEM observation the impurity phase of $Ce_{0.5}Nd_{0.5}O_{1.75}$ (CNO) was also identified as a result of the decomposition products of the NCCO phase due to evaporation loss of Cu for the deposition at high temperature. The (004) and (008) peaks of the CNO phase appears to precisely coincide the (110) and (220) peaks of the NCCO phase at 2 = 32.5° and 68.2°. According to the above facts, these two additional peaks in the XRD spectra in Fig. 3a may dominantly relate to (110) and (220) planes of the NCCO phase, whilst those in Fig. 3b closer to (004) and (008) planes of the CNO phase. According to the peak intensity, the volume fraction of impurity phase (CNO) and/or non-c-aligned components of the NCCO decreased by 15% for the film deposited at 820°C compared to that at 780°C.

Regarding superconductivity, films grown at temperatures below 750°C were generally not superconducting, despite the prolonged post-annealing in vacuum. Further, the films deposited at higher temperatures show superconductivity with Tc between 15 K and 20 K. The higher deposition temperature tends to produce film with higher Tc. It is interesting to have a look at the surface damage of the films generated by oxygen reduction during the annealing process in vacuum. For this purpose, a set of SEM images taken from the films deposited and annealed at various temperatures is depicted in Fig. 4. One can see serious damages generating defect structures with diameters up to

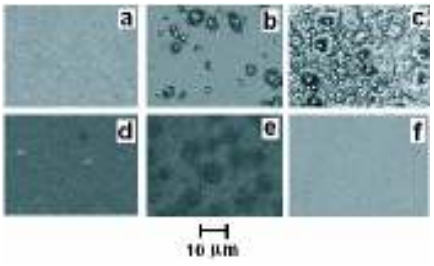

FIG. 4: The SEM images of films with deposition temperature (Td), annealing temperature (Ta) and duration (ta) : a). Td = Ta = 780°C, ta = 5 min, b). Td = Ta = 780°C, ta = 30 min, c). Td = Ta = 780°C, ta = 45 min , d). Td = Ta = 680°C, ta = 10 min , e). Td = Ta = 820°C, ta = 5 min , f). Td = 820°C, Ta = 750°C, ta = 5 min.

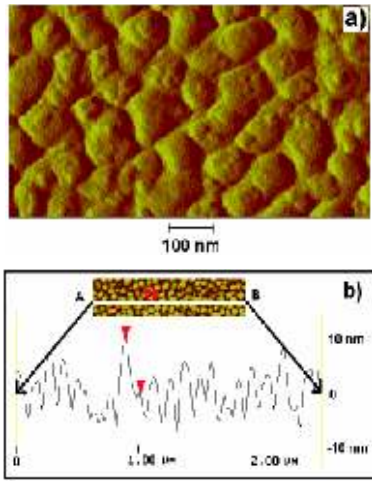

FIG. 5: a). An AFM image taken from of the same NCCO film presented in Fig. 4f, b). the result of section analysis marked by A and B along 2.5 μm.

10 μm on surfaces of the films annealed in long period (Fig. 4b and 4c) and at higher temperature (Fig. 4e), although these films are superconducting. Contrarily, films annealed in shorter duration (Fig. 4a) and at lower temperature (Fig. 4d) have much smoother surfaces. All the above-mentioned films have been deposited and annealed at the same temperatures. We have apparently succeeded to obtain a smooth film grown at 820°C and annealed at 750°C for 5 minutes as shown in Fig. 4f. Growing film at higher temperature is crucially required from the viewpoint of enhanced superconductivity as indicated by higher Tc, since oxygen atoms can fully occupy the apical sites during the deposition process. Besides, the growth of non-c-aligned components of the film is also suppressed at high temperature. The annealing procedure at lower temperature, on the other hand, is expected to induce a smooth film surface.

We further explore the grain morphology using a contact mode AFM observation on the same film as that exhibited in Fig. 4f. The grain structure looks densed and homogeneous with respect to their shape and size, as can be seen in Fig. 5a. The grain size varies from 60 up to $\sim$100 nm, signifying that the film is constituted by nanocrystals. Moreover, according to the AFM section analysis along the straight line between A and B (2.5 μm long) as presented in Fig. 5b, the "topography" of nanocrystals nicely characterizes a row of grains with vertical steps in the range from -10 nm to 10 nm being relative to the mean level (zero position), yielding an average roughness of 3.5 nm. This roughness is low enough rendering the film to be appropriate for the use of junction fabrication, as already implemented for fabrication and structuring of ramp-typed junctions [7] and junctions parallel to the c-axis [15].

IV. SUMMARY

To summarize, fabrication of the c-aligned NCCO films on the STO substrate employing PLD technique has been described in this paper. Films having Tc of 20 K with smooth surface were produced by the deposition at 820°C and in-situ post-annealing at 750°C for 5 minutes in vacuum. The corresponding films with the thickness of 150 nm are constituted by nanocrystaline grains having size of less than 100 nm and average roughness of 3.5 nm.

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