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Microstructural Study in Heteroepitaxial YBa₂Cu₃O₇/Nd₂CuO₄ Multi-Layers by Using Electron Microscopy

J. Gao, Y. L. Cheung, and S. M. So

Abstract—Neodymium copper oxide Nd₂CuO₄ (NCO) has been applied as a buffer material to improve the epitaxy of YBa₂Cu₃O₇ (YBCO) thin films on reactive substrates and as a potential barrier to construct multi-layer junctions. The microstructures and interfaces in heteroepitaxial Nd₂CuO₄/YBCO multi-layer have been characterized by using an electron microscopy. Cross-sectional images obtained on a transmission electron microscopy (TEM) revealed an atomically sharp boundary between layers, underlining the excellent compatibility of NCO with YBCO. No chemical reaction occurred between film and substrate. It was found that all layers grow highly epitaxially with their *c*-axis perpendicular to the substrate surface. On the other hand, various defects such as mis-oriented grains and stacking faults were found near the interfaces.

Index Terms—Nd₂CuO₄, superconducting films, TEM.

I. INTRODUCTION

NEODYMIUM copper oxide Nd₂CuO₄ (NCO) with a 214T' structure has been introduced as a new buffer material to improve the initial epitaxy quality and surface morphology of YBCO thin films grown on yttrium stabilized ZrO₂ (YSZ) [1], [2]. Such a NCO material was first reported in 1973 [3], which has a very stable tetragonal structure with lattice constants $a = 3.94 \text{ \AA}$ and $c = 12.50 \text{ \AA}$. It behaves as a semiconductor with a high value of resistivity at low temperature. For an appropriate buffer layer, it must be inert both chemically and structurally. Moreover, it should provide a lattice strain relief and a high chemical stability [4]. Compared with those 123-phase compounds, the 214-phase compounds show a higher stability in their crystal structure and physical properties. There is no phase transition below the deposition temperature or when the oxygen content changes. The lattice constant of NCO matches well with that of YBCO. The thin films of NCO always show excellent crystallinity and very smooth surface. All these features make NCO a good buffer material for growing YBCO on reactive substrates. Recently, we also succeeded in applying NCO as a barrier to construct high- T_c Josephson junctions with high R_n values [5].

The interfaces and microstructures in the heteroepitaxial multi-layer can greatly affect the initial epitaxy and the crystallinity of the grown layers. For instance, it has been known that the crystallinity and superconductivity of YBCO film

deposited on YSZ could be hampered by the intermediate layer formed at the YBCO/YSZ interface. For multi-layer junctions, the boundary between electrode and barrier is a crucial factor to determine the performance of the formed junctions. A poor interface is usually caused by the structural, thermal and chemical incompatibility between materials. Such interfacial and structural defects can be well identified by transmission electron microscopy (TEM). Hence, the study in interfaces and microstructures is of significance for many researches based on multi-layers.

In this paper, the detailed structures of heteroepitaxial multi-layer of YBCO/NCO have been investigated by means of TEM. The cross-sectional TEM (XTEM) study gives insight into the nature of epitaxial growth and interface structures. The goal of our study is to reveal the possible origins which cause the degradation in both crystallinity and superconductivity. In particular, the structural compatibility between these two compounds is discussed.

II. EXPERIMENTAL

YBCO and NCO thin films were fabricated on a STO substrate by using an off-axis rf-magnetron sputtering technique [6]. In brief, sintered stoichiometric discs of YBCO and NCO with diameter 50 mm and thickness 4 mm were used as sputtering targets. The chamber was evacuated with the background pressure lower than 5×10^{-6} mbar. The sputtering took place in a mixture gas of argon and oxygen with a ration of Ar:O₂ = 3 : 1. The sputtering pressure was kept about 1.6×10^{-1} mbar during the deposition. RF power of 80 W with a power density of 4 W/cm^2 was applied to the cathode. The substrate was mounted on the heater by using silver paste and the substrate temperature was kept at 750°C. After the deposition, the film was annealed at 500°C in 1 bar oxygen for 30 minutes.

To prepare cross-sectional TEM sample, tri-layer sample was cut and glued together face-by-face using epoxy. The sample was mechanically ground down to 10 μm in thickness by disc grinder (Gatan model 623) after the glue was dry. The sample was mounted on a single hole Mo grid and was further thinned by Ar ion milling with two ion-beam blocks to protect the films. During ion milling, the ion-milling holder was rotated and two ion guns were used. The sample was tilted with the beam incident angle of $\sim 15^\circ$. The applied beam energy was about 5 keV and beam current was kept as 0.5 mA. When color fringes could be observed, the ion milling could be changed into an ion polishing procedure. The ion polishing was performed with the

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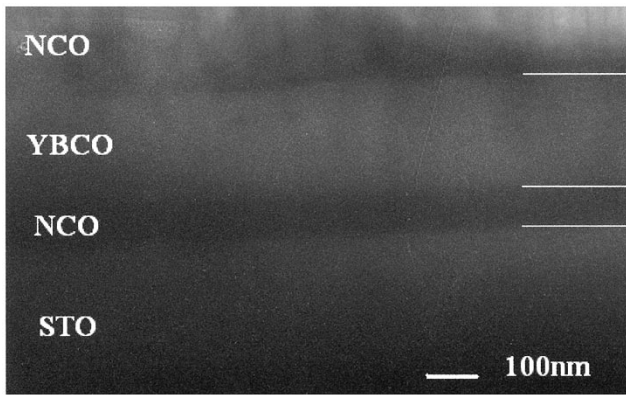


Fig. 1. Low-magnification XTEM image of NCO/YBCO/NCO tri-layer grown on STO substrate.

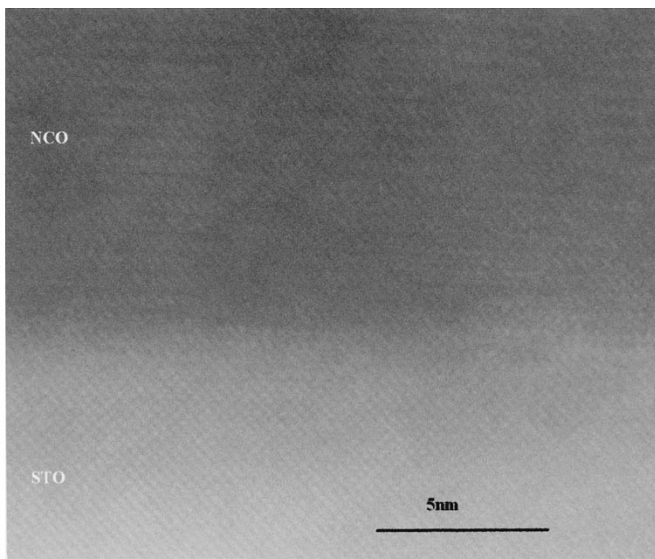


Fig. 2. Interface between the NCO buffer layer and STO substrate.

tilting angle of 8° – 10° , the beam energy ~ 3 – 4 keV and the beam current ~ 0.3 mA.

Electron micro-images were observed on a Tecnai 20 transmission electron microscope with 200 kV.

III. RESULTS AND DISCUSSION

To be sure the observations made in this study are reliable and reflect the common features of YBCO/NCO heteroepitaxial multi-layer, five samples made by different processes were examined. Fig. 1 gives a low-magnification overview of a NCO/YBCO/NCO tri-layer. The sample was prepared using an off-axis sputtering technique. The three different layers could easily be identified by their different image contrast. All layers were rather uniform and single crystal like. Strain effects due to lattice mismatch were unlikely appeared as the TEM image shows a sharp contrast for each layer. The layer thickness measured from TEM image agreed well with that estimated from the deposition time.

Understanding the interfacial microstructures between films and substrates is very important because it may precisely control the growth process [7]. In general, the features of the inter-

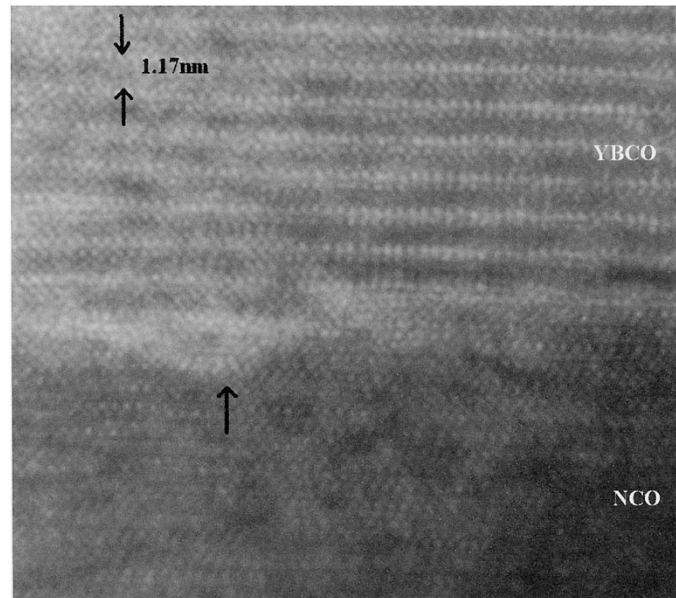


Fig. 3. Interface between the YBCO and NCO. A few tiny anti-domains appeared near the interface, as indicated by an arrow.

face could be mainly controlled by three factors including the chemistry of the join compounds, the growth kinetics and the presence of defects [4]. Since both chemical and structural compatibility between NCO and STO were very good, the resulted NCO/STO interface was well defined. Fig. 2 shows NCO grown on STO substrate epitaxially with the c -axis perpendicular to the STO surface. The NCO layer could be easily distinguished from the adjacent STO substrate. From Fig. 1, the surface of STO was quite smooth without any considerable steps. It has been recognized by *in-situ* resistance measurement that the initial growth of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, also of the 214T' compound, on YSZ surface could be layer-by-layer [8]. The early formation of NCO on STO has not been investigated, but it had to be similar to that for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. On the other hand, although the structure of NCO matches well with STO (both are perovskite oxides and their lattice mismatch is $\sim 1\%$), some defects were still visible near the interface, such as mis-oriented grains and misfit dislocations. They might be due to the growth kinetics at the initial growing stage. Defects on the substrate surface propagate as defects in the c -axis oriented films. Therefore, good quality of substrate is also a main factor to grow defect-free films.

To obtain an excellent epitaxy and crystallinity in the subsequently grown YBCO film, the surface of the base material must be extremely smooth. Observed under a scanning electron microscopy (SEM) and atomic force microscopy (AFM), the surface of NCO layer is very flat and smooth. It ensures the quality of grown YBCO and the formed interface. Fig. 3 demonstrates high resolution TEM (HREM) image of the NCO/YBCO interface. It was sharp and atomically flat. YBCO thin film was grown well oriented and crystallized on NCO. Except for a few tiny anti-domains (about 2 nm in size) in the NCO layer close to the NCO/YBCO boundary, no considerable defects could be found. These anti-domains might act as nucleation centers with an unwanted orientation if they were further developed. However, as the growth continued, such tiny anti-domains became

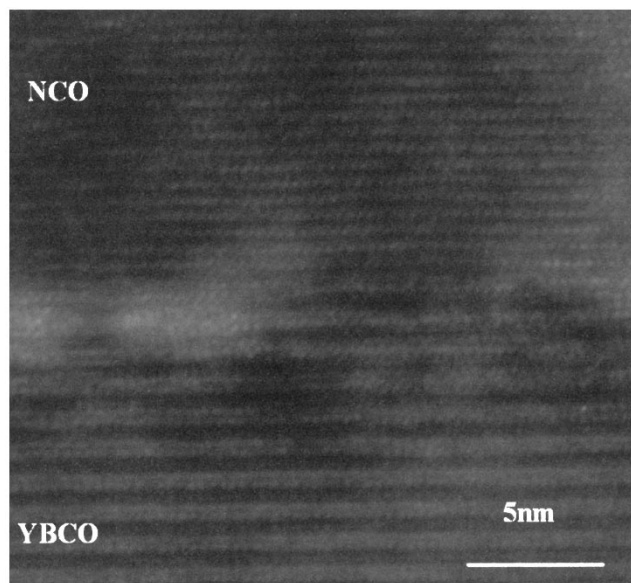


Fig. 4. Interface of YBCO layer and up NCO layer. Mis-oriented grains could be found in NCO layer near the NCO/YBCO boundary.

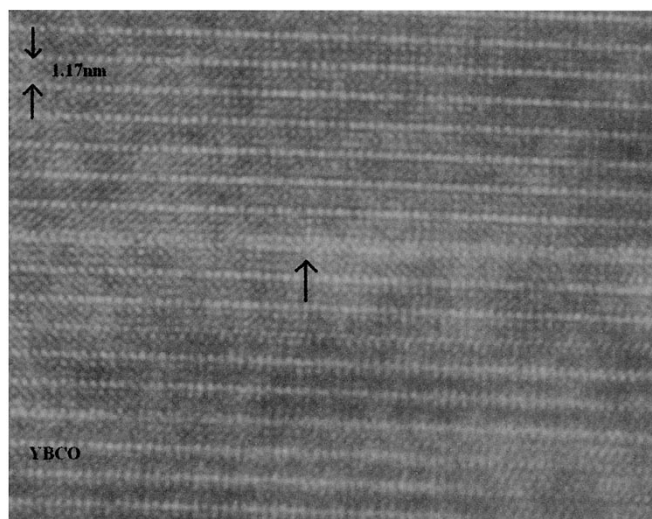


Fig. 5. HREM image of YBCO layer, stacking faults were quite common present near the NCO buffer/YBCO layer interface.

extinct and were covered by the YBCO film with the desired orientation. This was similar to what we observed on coherently tilted YBCO films with a (105) orientation [9].

A high-resolution TEM (HREM) image of the NCO/YBCO interface is shown in Fig. 4. In comparing with the YBCO/NCO interface, the interface formed by growing NCO on YBCO surface was relatively poor, although the interface was still clear and sharp with an atomic scale. Stacking faults could be seen at the boundary. Mis-oriented grains in the local area of NCO layer were also formed. It was not clear that such grains were caused by film growth or by the ion-milling process.

The microstructure and defects formed in the YBCO film grown on NCO surface were studied. The epitaxy and crystallinity in the YBCO film are of high quality (see Fig. 5). The YBCO layer was well epitaxially grown with the c -axis orientation. No big defects like grains or dislocations could

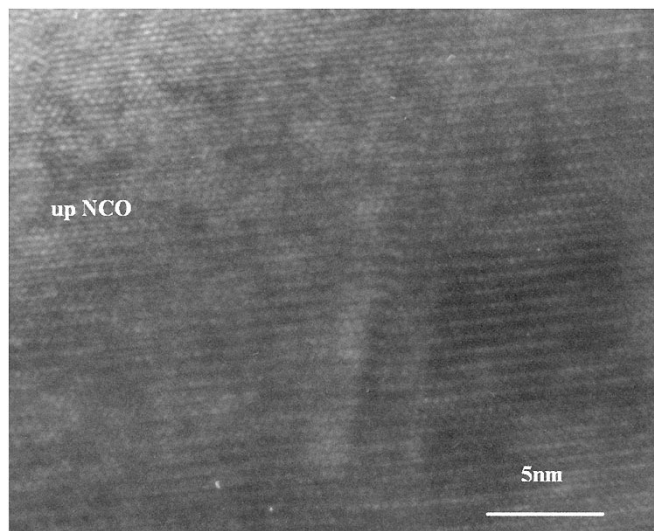


Fig. 6. HREM image of the NCO layer grown on YBCO. In comparing with the YBCO layer deposited on NCO, the growth of NCO is relatively poor and more defects could be seen.

be found under the electron microscope. Most of the defects appeared near the NCO buffer layer/YBCO layer interface. Stacking faults were the most common defects in YBCO thin film. It is well known that stacking faults may be produced by excess Cu-O layers. After the initial growing stage, the YBCO film was almost free of defect. Thus, the defects in YBCO might be caused by the interface only.

The quality of the NCO film grown on the YBCO surface was found relatively poor in comparing with the NCO layer directly grown STO, which might be caused by the relatively poor surface of the YBCO. Our experiments proved that the NCO films always show an extremely smooth surface, which ensures the high quality growth of YBCO [1]. In the NCO layer deposited on YBCO, more defects such as mis-oriented grains and dislocations, as shown in Fig. 6. Similar to the case for YBCO grown on NCO, most of defects were near the NCO/YBCO interface.

The microstructure study demonstrates that the epitaxial growth of YBCO can be significantly improved by such a NCO buffer layer. The NCO material with a 214T' structure is well compatible with YBCO material. It can serve as a good buffer layer or barrier material for various applications.

IV. CONCLUSION

Microstructures and interfaces in the heteroepitaxial YBCO/NCO multi-layer have been characterized by means of transmission electron microscopy (TEM). The HREM results show that both YBCO and NCO layers are grown epitaxially with c -axis orientation. The YBCO/NCO interface is very clear and atomically sharp. A few tiny mis-oriented structures can be seen, but the further growth of such grains is effectively depressed by the film growth along the c -axis. The interface formed by grown NCO on YBCO surface is relatively defective. For all the samples that we studied, both interfaces and bulk films are free of amorphous layers and secondary phase particles. The results demonstrate the excellent compatibility between NCO and YBCO.

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