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Characteristics of $YBa_2Cu_3O_7$ Thin Films Deposited on Substrates Buffered by Various TiO_2 Layers

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Titanium nitride (TiN) and superconducting $YBa_2Cu_3O_7$ (YBCO) thin films have been deposited sequentially on $SrTiO_3$(STO)(100) substrates by *in situ* pulsed laser ablation. The TiN films were originally intended to serve as the lower contact electrode of the *c*-axis YBCO thin films. It was found that, although high-quality YBCO films could be obtained with the YBCO/TiN/STO(100) bilayer structure, the TiN(100) layer was oxidized which changed the structure into YBCO/TiO_2/STO(100) during YBCO deposition. Comparative studies of depositing YBCO films directly onto a dc-sputtered TiO_2/STO(100) template conventionally used in the selective epitaxial growth (SEG) process have, however, resulted in formation of a nonsuperconducting YBCO top layer. The characteristics of the resultant TiO_2 layers obtained using various processes were analyzed to delineate the apparent discrepancies.

KEYWORDS: TiN films, oxidation of TiN, pulsed laser deposition, YBCO/TiO_2/STO bilayer structure, selective epitaxial growth process

TiN thin films have been studied and used extensively in recent years due to their superior mechanical, thermal, and electrical properties.[1–3] Moreover, it has been suggested that TiN thin films not only serve as buffer layers in depositing superconducting $YBa_2Cu_3O_7$ (YBCO) thin films on various substrates such as Si, Hastelloy, Inconel and stainless steel, but also as the electrode for metallization and integration of superconductor and semiconductor devices.[4,5] In the light of these unique properties exhibited by TiN films, we previously attempted to fabricate the YBCO/TiN/substrate structure by sequential *in situ* pulse laser deposition (PLD) to investigate the out-of-plate (along *c*-axis) transport properties of YBCO thin films. Surprisingly, we were unsuccessful because of the oxidation of TiN layer during the deposition of YBCO thin films. The reaction of TiN films with oxygen is thermodynamically favorable.[6,7] Insulating and transparent TiO_2 films with a rutile structure were formed immediately at a temperature of about 800°C. Since oxidation is unavoidable during deposition of YBCO films, the originally considered YBCO/TiN/substrate bilayer structure should be an YBCO/TiO_2/substrate bilayer structure instead. It seems reasonable to conclude at this point that, even though our attempts at using TiN films as an electrode were unsuccessful, the resultant TiO_2 films can still serve as an excellent buffer layer for growing YBCO films on some technologically important substrates.

There, however, exist some apparent discrepancies with this conclusion and the results demonstrated in the recently developed selective epitaxial growth (SEG) process.[8,9] In this method, a detrimental template material was deposited and prepatterned on a bare substrate. Then the subsequent YBCO films growing on top of this template layer become insulating, while those growing directly on the substrate have superconducting characteristics. Damen *et al*.[8] and Cheng *et al*.[9] have used the patterned Ti template for selective epitaxial growth of microsized YBCO structures. The YBCO thin film grown on regions covered by the oxidized Ti layer became amorphous and exhibited insulating characteristics, while those deposited directly on bare STO substrate regions showed excellent superconductivity. Recently, Chuang *et al*.[10] have prepared a dc-sputtered TiO_2 layer directly as the selective masked template on a bicrystal $SrTiO_3$ (STO) substrate to *in situ* fabricate dc superconducting quantum interference devives (SQUID). Again, the TiO_2 layer exhibited excellent selectivity for growing nonsuperconducting YBCO films. In order to resolve these apparent inconsistencies, efforts have been taken to examine the crystallinity, surface morphology, interface, and electronic structure of these films.

Both the TiN and YBCO films have been prepared by PLD. The detailed description of the PLD system was reported previously.[11] Briefly, a KrF excimer laser operating at a repetition rate of 3–8 Hz with an energy density of 2–5 J/cm^2 was used. In order to *in situ* fabricate the YBCO/TiO_2/substrate structure, both YBCO and TiN targets (99.9% pure) were installed in the deposition chamber simultaneously. It was found that the optimum deposition conditions for the TiN films were obtained under the background pressure ($\sim 5 \times 10^{-6}$ Torr) and at a substrate temperature $T_s = 700$°C. On the other hand, the optimum deposition conditions for the YBCO films deposited on STO were obtained at an oxygen partial pressure of 0.3 Torr and $T_s = 780$°C.[11]

The dc-sputtered TiO_2 films were prepared by a laboratory-built sputtering system. A 50-mm-diameter (99.9% pure) titanium disk was used as the target. The distance between the target and substrate was about 25 mm. Sputtering was carried out in a 1:29 oxygen/argon mixture at a total pressure of 0.2 Torr. Since the substrates were not intentionally heated during deposition, the as-deposited films were amorphous. TiO_2 films of 20–50 nm thickness were deposited at a typical deposition rate of 0.1 nm/min using a total dc input power of 30 W.

The electrical properties of the TiN and YBCO films was measured using a four-probe method. The crystalline structure of the films was examined by X-ray diffraction (XRD, Rigaku D/max-rc/ru200b) using Cu Kα radiation. The surface morphology of the films was observed by atomic force microscopy (AFM, Digital Instruments DI 5000) and scanning electron microscopy (SEM).

The as-deposited PLD-TiN films, typically about 30–80 nm thick, were shiny golden yellow in appearance. Curve (A) in

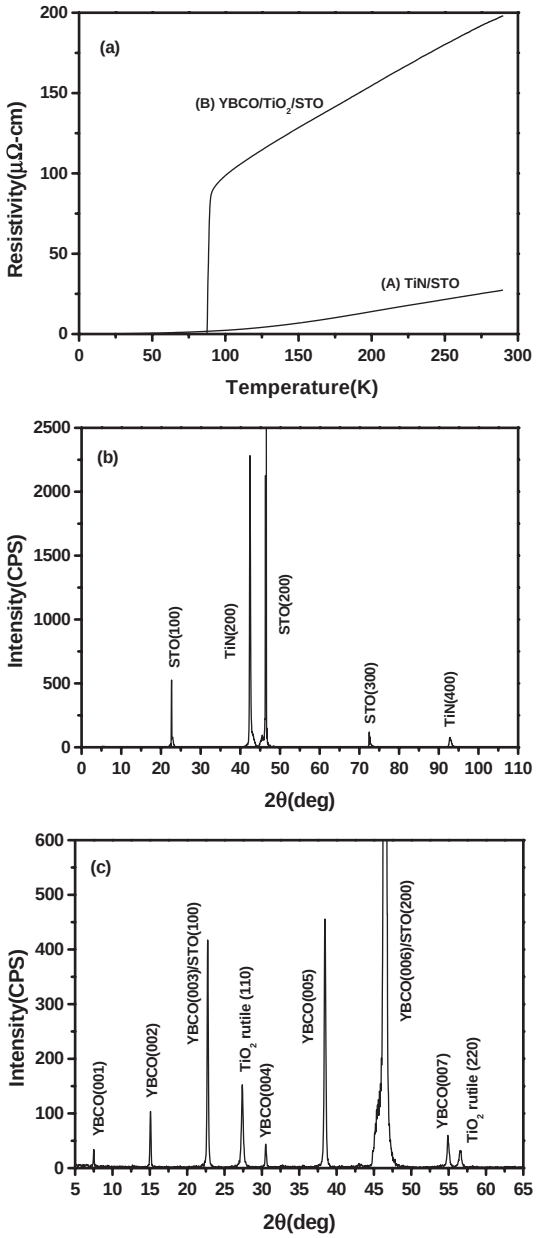

Fig. 1. (a) Resistivity versus temperature curves of a PLD-TiN film (curve (A)) and a YBCO/TiN bilayer structure (curve (B)) deposited on (100)STO substrates; (b) XRD pattern of the (100)TiN film; (c) XRD pattern of the YBCO/TiN/STO structure.

Fig. 1(a) shows the resistivity versus temperature (R-T) curve of an 80-nm-thick TiN film on STO. It is evident that the as-deposited TiN is an excellent metallic compound with a nearly zero residual resistance below 20 K, indicative of almost impurity-free crystallinity. Figure 1(b) shows the XRD pattern of the film, indicating that the TiN film has grown with a predominance of (100) texture. The surface morphology as revealed by AFM, shows an average grain size of about 50 nm with a rather smooth surface. The root mean square (RMS) roughness of the surface was estimated to be about 0.2 nm.

The high-quality TiN thin films with an excellent electrical property and a smooth surface described above seem very suitable as a conductive buffer layer for growing YBCO thin film. Therefore, we prepared a bilayer structure by depositing TiN and YBCO layers sequentially on STO substrates. The thicknesses of TiN and YBCO layers were approximately

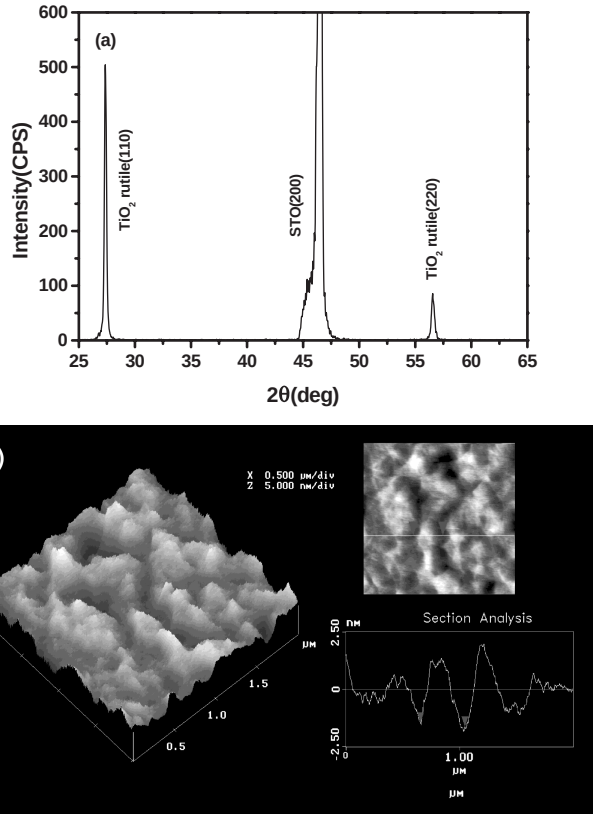

Fig. 2. (a) XRD pattern and (b) AFM image of PLD-TiN transferred TiO_2 films. The scanned area of the AFM image was $2\,\mu m \times 2\,\mu m$ and the dark-to-light vertical scale was 5 nm.

50 nm and 200 nm, respectively. Figure 1(c) shows the XRD pattern for the YBCO/TiN bilayer structure formed on the STO(100) substrate. Strong (00l) diffraction peaks of YBCO can be observed, indicating that the YBCO film grew with a *c*-axis-preferred orientation. The YBCO overlayer shows virtually the same transport properties of typical good-quality single-layer YBCO films with a zero-resistance temperature (T_{co}) of 88 K (Curve (B) in Fig. 1(a)).

However, despite the success of growing an YBCO/TiN/STO bilayer structure, the effect of oxidation on TiN films was apparently overlooked. Since the *in situ* deposition of YBCO films is usually performed in oxygen ambient at a high temperature, one would have wondered whether any degradation of TiN took place in such an environment. To verify the suspicion, we etched off the top YBCO layer and found that the gold-colored conductive TiN layer no longer existed. Instead, the original TiN layer has turned into a transparent insulating layer. In order to identify the resultant product, a 50-nm-thick TiN film was loaded into the experimental chamber and treated at 780°C for 6 min with an oxygen partial pressure of 0.3 Torr to simulate the YBCO film deposition process. Figure 2(a) shows the XRD result for the oxidized TiN films. The diffraction peaks are identified as that of the rutile TiO_2 with the (110)-preferred orientation. The full-width at half-maximum (FWHM) of the $TiO_2(110)$ θ–2θ diffraction peak was about 0.21°. This unexpected result suggests that TiN might not be a good underlayer electrode since oxidation is unavoidable during deposition of YBCO. The AFM image in Fig. 2(b) illustrates that the grain size of TiO_2 thus obtained is about 400 nm, which is much larger than that of the original

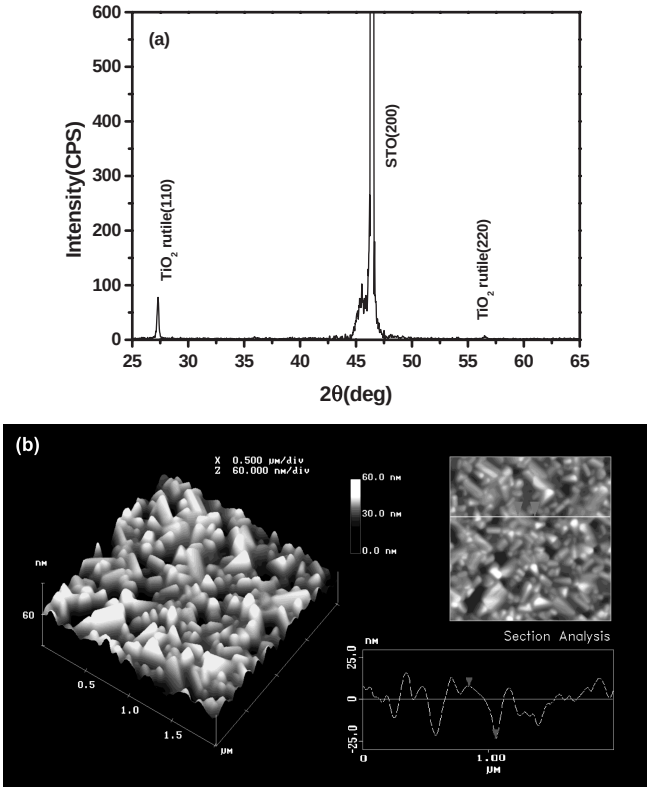

Fig. 3. (a) XRD pattern and (b) AFM image of annealed sputtered TiO_2 film. The scanned area of the AFM image was $2\,\mu m \times 2\,\mu m$ and the dark-to-light vertical scale was 60 nm.

TiN films. A greater variation in roughness (RMS roughness $\sim$1 nm) can also be observed in the figure.

As was already pointed out, very contrary experimental results were observed for YBCO films grown using the SEG technique. Smooth, black, and good superconducting properties were obtained for YBCO films grown on the STO substrate directly, whereas rough, nearly transparent, insulating YBCO films (typical resistivity at room temperature $>10^5\,\Omega\cdot$cm) with large particulates were obtained for YBCO films grown on TiO_2 buffer layers. For the latter structure, the absence of an YBCO diffraction peak in XRD measurement indicates that the material is amorphous. It is then interesting to distinguish the differences between TiO_2 films prepared by dc sputtering and those transformed from PLD-TiN films. In order to simulate the change of amorphous TiO_2 films prepared by dc sputtering prior to YBCO deposition, a 50-nm-thick sputtered-TiO_2 film was loaded into a vacuum chamber maintained at 780°C with a 0.3 Torr oxygen pressure for 6 min. Figures 3(a) and 3(b) show the XRD and AFM images of the annealed sputtered TiO_2 film, respectively. As shown in Fig. 3(a), the diffraction peak of the (110)TiO_2 rutile phase indicates that the amorphous sputtered TiO_2 film was transformed into the same rutile phase as that of the PLD TiN-transferred TiO_2 under the same annealing conditions. However, the relatively weak diffraction intensity and broad FWHM ($\sim$0.33°) suggest that the crystallinity of these annealed sputtered TiO_2 films may not be as good as that of TiN-transferred TiO_2 films. The AFM image in Fig. 3(b) further reveals that the film consists of many small crystals with irregular facets. The RMS roughness of this film was about 9 nm as compared to 1 nm for the oxidized TiN film.

It is known that the growth of epitaxial YBCO films is closely related to the initial stages of deposition as nucleation and growth first occur on the substrate, as well as to the formation and evolution of dislocation and other defects as deposition proceeds. Therefore, the structural properties and the surface morphology of the substrates can influence the final quality of the deposited films significantly. Comparing the XRD and AFM results shown in Figs. 2 and 3 respectively, it seems likely that the poor crystallinity and much higher RMS roughness of annealed sputtered TiO_2 films might be responsible for quenching the superconductivity of YBCO films grown on it. Alternatively, another interface layer formed during YBCO deposition might also be possible. In this scenario, a thin $BaTiO_3$ layer formed immediately after the first deposition of YBCO can be crucial for subsequent growth. Whether the interfacial layer is crystalline $BaTiO_3$ or amorphous Ba–Ti–O layer[8] could make significant differences. Experiments including Auger electron spectroscopy (AES) depth profile analyses and interficial X-ray absorption spectroscopy for determining the possible interactions occurring at the YBCO and TiO_2 interface are currently in progress and will be reported separately.

In summary, TiN thin films grown on the $SrTiO_3$(100) substrate by PLD are demonstrated to be a suitable template for growing YBCO films. However, although the TiN films originally possessed excellent electrical properties, these failed to serve as the underlayer electrode in an YBCO/TiN/STO bilayer structure since it was readily transformed to rutile(100) TiO_2 films during the deposition of top-layer YBCO films. In contrast to the good superconductivity obtained in the YBCO/TiN-transferred TiO_2/STO structure, YBCO films grown directly on a TiO_2 layer prepared by dc sputtering, turned out to be insulating. The results suggest that poor crystallinity and a drastic increase in RMS roughness of the annealed sputtered TiO_2 films might have direct influences on growing stoichiometric YBCO films. Experiments aimed at resolving the possible interface layer modifications are in progress and are expected to provide more insight on this matter.

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