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Formation of outgrowths at the initial growing stage of $YBa_2Cu_3O_x$ ultrathin films on ZrO_2 substrates

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Ultrathin films of $YBa_2Cu_3O_x$ with good crystallinity and superconductivity were prepared by a modified off-axis sputtering. The microstructure, with emphasis on surface morphology and formation of outgrowths, was studied by using atomic force microscopy and electron microscopy. It was found that many outgrowths were formed at the initial growing stage. Therefore it is important to suppress the nucleation of outgrowths at a very early growing step to obtain a smooth film. The nucleation of outgrowths is significantly influenced by surface defects on the substrate. Discussion is also made in correlation with the occurrence of an intermediate layer commonly observed on ZrO_2. From our observation, $YBa_2Cu_3O_x$ might be grown directly on the surface of ZrO_2 without forming any intermediate layer, if the film thickness is very small. © *1995 American Institute of Physics.*

Very smooth $YBa_2Cu_3O_x$ (YBCO) thin films are of great interest for the development of high-temperature superconducting devices. However, the surface morphology of YBCO thin films often does not satisfy the requirement of device engineering, although much effort has been made to improve the surface quality of YBCO films in the past several years. Studies reported so far have proven that many factors such as the quality of substrate, lattice mismatch between film and substrate, and deposition parameters like plasma current, would significantly affect the surface topography.[1–3] Not much attention has been focused on the origin and nucleation of the surface defects. For yttrium-stabilized ZrO_2 (YSZ) substrates, the formation of outgrowths is further complicated due to the occurrence of an intermediate layer, mainly $BaZrO_3$ (BZO).[4,5] Presently, the control of surface morphology proceeds on an empirical basis, mainly by optimization of deposition parameters, and a basic understanding of the formation of surface defects is still lacking.

In this letter we report investigations on the origins and initial formation of the outgrowths on YBCO films sputtered on YSZ. The major point of interest concerning the presented research is to clarify the formation and origins of the surface defects, hence we can mostly depress them at the initial growing stage. The study was carried out on ultrathin films with a thickness down to 2 nm.

The samples were prepared by using a modified off-axis rf-magnetron sputter technique as published previously.[6] X-ray diffraction was performed for most samples and the spectra reveal broadened but clear (00*l*) peaks of the films demonstrating *c*-axis orientation even at the initial stage of growth. The crystallinity of these ultrathin films was evaluated by the full width at half maximum of the rocking curve $\Delta\omega$, and the minimum yield of He-ion channeling $\chi_{\min}$. The value of $\Delta\omega$ of the (005) peak for films with thicknesses ranging from 8 to 80 nm is between 0.21° and 0.40°, indicating a good crystallinity and high *c*-axis orientation. The rocking curve was found to significantly broaden as film thickness increased. The increase of the mosaic spread could be due to the large lattice mismatch of 7% between YSZ and YBCO. The aligned He-ion channeling gives a minimum yield $\chi_{\min} \sim 20\%$. Such a value of $\chi_{\min}$ is reasonable for an ultrathin film of YBCO on YSZ and comparable to those measured on ultrathin films so far by other groups.[3,7,8]

The critical temperature (T_c) of our thin and ultrathin films is shown in Fig. 1. For film thicknesses down to 10 nm, full transitions between 87 and 90 K have been obtained. Degradation of T_c has been found on ultrathin films with thicknesses less than 10 nm. For films thinner than 4 nm, the transition curve still exhibited a metallic behavior but no T_c could be found above 20 K. The normal state resistivity of ultrathin films turned out to increase rapidly when the film thickness decreased. On the other hand, the normal state resistivity of relative thicker films (>10 nm) was about 40–100 $\mu\Omega$ cm, which is comparable with that obtained on a single crystal of YBCO. The obtained results demonstrate good quality of our thin and ultrathin films.

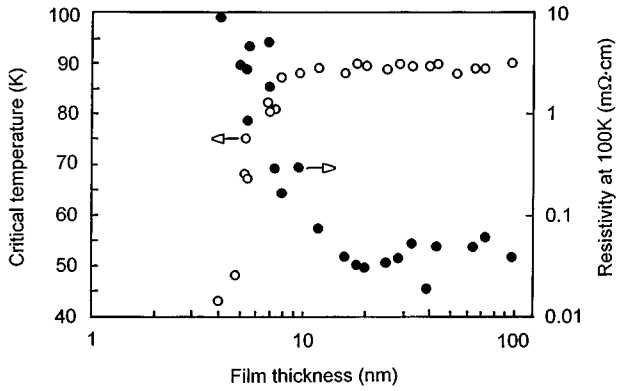

FIG. 1. The critical temperature and normal state resistivity as functions of the film thickness. No significant degradation in the critical temperature has been found when films are thicker than 10 nm.

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The surface of YBCO films can be rough sometimes, although the films showed a good superconductivity. The surface roughness may result from out-of-plane *c*-axis growth, surface outgrowths, and isolated clusters of *a*-, *b*-axis crystallites. The early stage of growth is of importance for the formation of these surface defects. To study the initial growth of the surface defects, atomic force microscopy (AFM) was carried out on a number of ultrathin films with thicknesses ranging from 2 to several tens of nm. It was found that outgrowths have already nucleated even at the initial growing stage. A typical initial formation and subsequent expansion process of outgrowths is shown in Fig. 2. Compared with the typical surface of a substrate shown in Fig. 2(a), it can be found that a YBCO layer almost fully covered the substrate although the average film thickness is only 2 nm. The film is not completely smooth and consists of interconnected islands suggesting that the film is still at the initial growing stage. Besides, some outgrowths with an average size of ~60 nm are visible. The height of these nuclei is 10–30 nm, which is also well above the average film thickness. Obviously the outgrowths grow much faster than *c*-axis oriented YBCO. The image obtained on a 4 nm film displays a similar feature but the lateral grown and island coalescence lead to a continuous layer and hence to a nonvanishing conductivity. The films at this stage exhibit a metallic behavior on the *R-T* curve and show a superconducting transition although the transition is not completed down to 20 K. Note that the scale of the horizontal axes is different from that in Fig. 2(b); the size of outgrowths on the 4 nm film is significantly enhanced. Thereafter, subsequent growth results in outgrowths with a typical size of ~200 nm distributed on the surface of final film of about 100 nm. The density of final outgrowth is lower than that of early nuclei, due to possible termination and/or combination of several nuclei. Our observation implies that the surface morphology of a thin film could be greatly influenced and determined by the first few minutes of initial growth.

A question raised here is: how are the films and outgrowths initially formed on the surface of YSZ? According to the report of Alarco *et al.*, the growth mechanism of YBCO on YSZ corresponds to the Volmer–Weber mode.[4,5] The deposited YBCO first nucleates on the substrate and forms small islands. Subsequently, these islands become larger in size and coalesce. However, the process is rather complicated due to the occurrence of the BZO intermediate layer. At present the formation of such an intermediate layer is not very clear. The HRTEM study on relatively thicker films (Fig. 3), as reported by others,[4] indicates that the interface between YBCO and BZO is well defined, whereas the interface between BZO and YSZ is quite rough showing a feature of interdiffusion. Most reported TEM studies so far reveal that the intermediate layer is typically more than 5 nm thick. In contrast, the HRTEM study on ultrathin YBCO films on YSZ made by using the same technique displayed a very clear interface and no intermediate layer could be observed.[9] It suggests that the growth of ultrathin and relatively thicker films on YSZ might be different due to different deposition processes. Typically, the deposition of ultrathin films takes only a few minutes. Then films are quickly cooled down to room temperature simply by turning off the heater. Within such a short period, the interaction between YSZ and YBCO would be very limited. In contrast, the

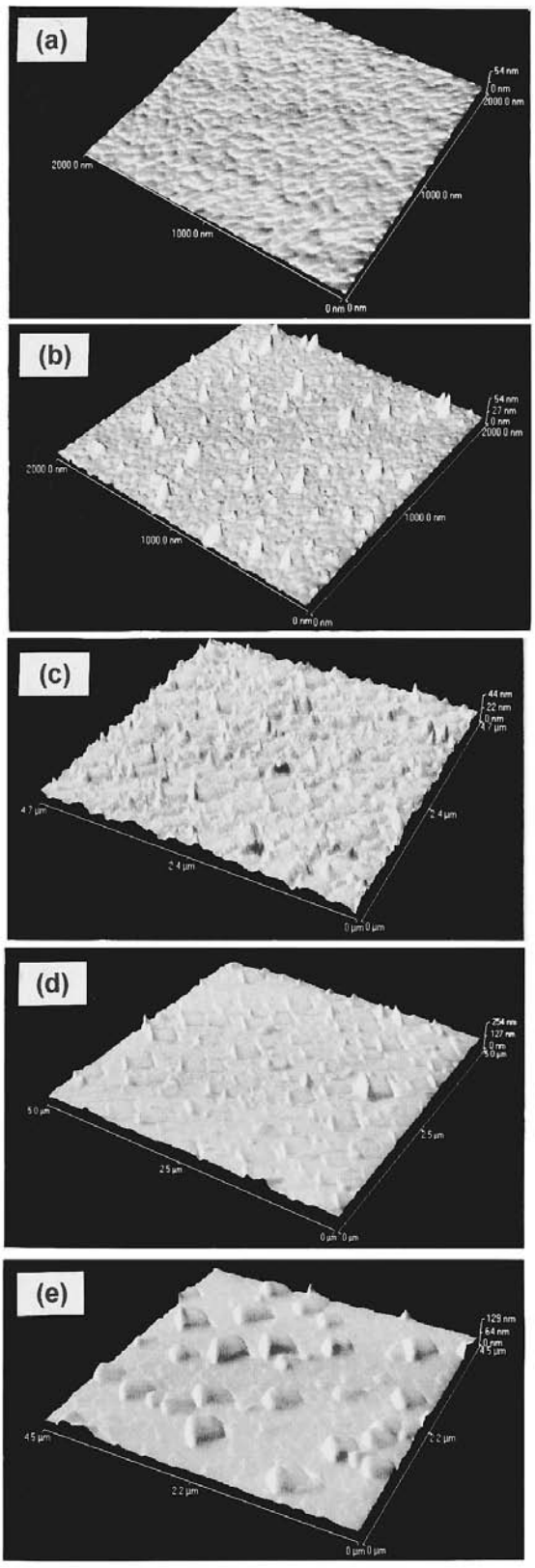

FIG. 2. The AFM images of surface of (a) an as-polished YSZ substrate; (b) a YBCO film with a thickness of 2 nm; (c) a YBCO film of 4 nm; (d) a film of 10 nm; (e) thin film of 50 nm. Please note that the scale of the horizontal axes for (a) and (b) are different from that of (c), (d), and (e).

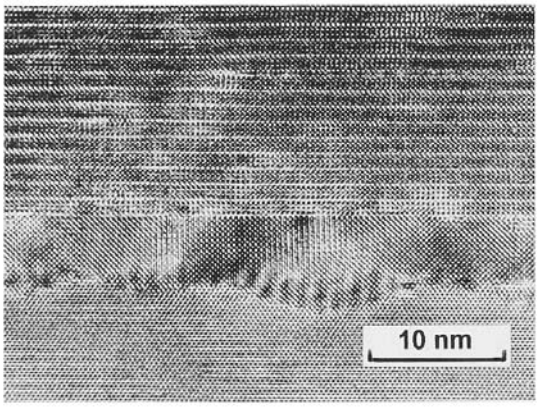

FIG. 3. Cross-sectional view by HRTEM of a YBCO film on the YSZ substrate. The film thickness is about 220 nm. An intermediate layer of 5–10 nm was formed.

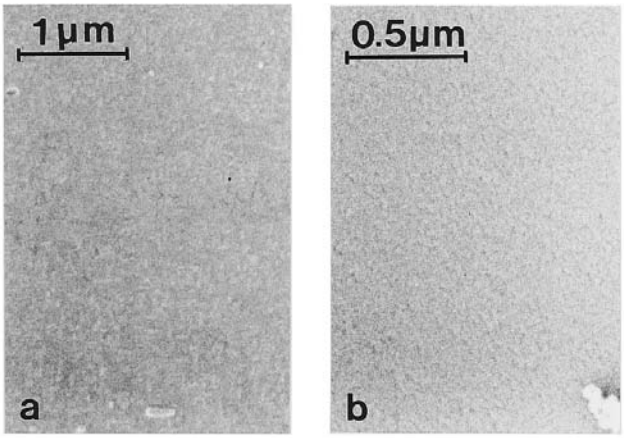

FIG. 4. (a) SEM image of an ultrathin film with a thickness of 8 nm grown on YSZ. The nucleation of the outgrowths was depressed. The transition temperature of this film is 86 K. (b) Surface morphology of a relatively thick film with a thickness of about 90 nm showing an extremely smooth surface and a transition temperature of 88.5 K.

deposition of relatively thicker films takes a much longer time with the substrate being kept at a high temperature. Thus significant interaction between YBCO and YSZ occurs resulting in an intermediate layer. It can be confirmed by the fact that high T_c and critical current density have been obtained on ultrathin films of 5 nm. If the BZO intermediate layer, which is typically thicker than 5 nm, was formed at the initial stage, it would not show a superconductivity. Thus we may conclude that the BZO intermediate layer is formed mainly due to the diffusion of Ba into YSZ during the long high-temperature deposition. Our results presented above demonstrated that both the YBCO *c*-axis layer and outgrowths would nucleate and grow directly on the YSZ substrate in the preparation of ultrathin films. Further detailed study on the interaction between YBCO and YSZ by using HRTEM is under way.

Chang *et al.* reported that outgrowths of CuO and *a*-axis grains could nucleate at the defects of dislocation configuration formed at the triple points where three grains meet during the final stages of coalescence to form a continuous film.[3] Our results have shown that many outgrowths are also formed at the initial growing stage. Therefore the nucleation of outgrowths can take place directly on YSZ. We have examined the surface of various YSZ substrates and found that substrates being repeatedly used mostly affect the formation of outgrowths. Such substrates usually also show a mirror-like surface but under a scanning electron microscope (SEM) some surface defects can be found. Energy dispersive x-ray analysis indicated these defects having composition different from YSZ. We found that to mostly suppress the outgrowths, substrates with a surface roughness less than 2 nm is required. In addition, the formation of outgrowths at the initial growing stage can also be influenced by the deposition parameters, such as substrate temperature T_s and growth rate. Using a lower T_s can significantly decrease the density of outgrowths. But a too low T_s could result in *a*-axis grains and degrade the superconductivity. In our case the optimized T_s is about 710 °C. The influence of oxygen partial pressure has been studied as well. According to our investigation, for making good ultrathin films the use of very high oxygen pressure in both deposition and cooling down processes should be prevented, although it may help to improve the surface smoothness of thicker films. By greatly suppressing the outgrowths at the initial stage, we found that the subsequent growth of YBCO on such a smooth initial layer led to an extremely flat surface, as shown in Fig. 4. Such YBCO films would be promising for many applications.

In conclusion, our results have shown that many outgrowths can be nucleated and formed at the initial growing stage. Therefore it is of importance to depress the formation of outgrowths at the initial growing stage. To make very smooth YBCO thin films on YSZ, the surface roughness of the substrate needs to be less than 1–2 nm. The occurrence of an intermediate layer between YBCO and YSZ may depend on the deposition process. Ultrathin films of YBCO can be grown directly on YSZ without forming an intermediate layer. Extremely flat and smooth YBCO films have been grown on the basis of a high quality initial layer.

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